OZONE

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A TREATISE OF ELECTRO-CHEMISTRY.

EDITED by BERTRAM BLOUNT, F.I.C., ETC.

OZONE

BY

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EDITOR'S PREFACE.

THE idea of a series of books on Electro-Chemistry emanated not from me, but from Messrs. Constable. Some years back I wrote for them a book called "Practical Electro-Chemistry," intended to cover a great part of the ground of knowledge then extant. Fortunately, knowledge has a habit of growing and of propagating its kind, and my book, in consequence of this, became a "back number".

The subject of Electro-Chemistry is so ramified and specialised that it was impossible for one man to make a survey of the whole field. This fact is the genesis of the present series in which those who have accurate and intimate knowledge of the various branches of electro-chemistry have undertaken the work for which they are particularly qualified. It will be readily understood that, as the series of books was started at an early period of the war, many contributors were engaged in work of national and primary importance, and were unable, however willing, to apply themselves at the moment to exacting literary work. But this difficulty was gradually overcome, as some prospect of a period to the struggle came within view, with the result which the reader will judge with consideration for the onerous conditions under which my contributors have wrought.

The monographs resulting from their labours speak for themselves, and if the educational advantages which I have obtained from reading them during their passage through the press is shared by the public, I believe that the thorough and modern work of my friends and collaborators will be appreciated, and such faults as there be will be attributed to the person ultimately responsible—the Editor.

AUTHOR'S PREFACE.

EVER since the time of its discovery Ozone has attracted the attention of chemists, physicists, and industrialists alike. To the former it presented the first example of a gaseous allotrope of an element, differing from oxygen in many remarkable ways. The physicist frequently came in contact with the substance in his investigations on the conduction of electricity through air, whilst the industrialist was not slow to avail himself of an oxidising agent, unsurpassed in strength, leaving no objectionable material in its wake, and at the same time easy, if indeed somewhat expensive, to manufacture.

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The angle from which Ozone and its modes of preparation was regarded by these three different sets of investigators naturally varied, and an endeavour has been made in the following pages to summarise and correlate the many different references which are to be found scattered over a wide field of literature. The merest survey, however, was sufficient to indicate that our knowledge of Ozone, its properties and modes of formation, is exceedingly scanty. The industrialist is ever at hand with extravagant claims as to the utility of "electrified oxygen"; the evidence as to the chemical behaviour and properties of ozone is somewhat meagre and frequently conflicting, for example, the existence of the ozonates and of oxozone still awaits confirmation; whilst the hypotheses advanced to explain the mechanism of its formation, either chemical, thermal, electrolytic, or photo-chemical, are purely speculative. Ozone is generally produced by means of the silent electric discharge, the

Aladdin's lamp of synthetic chemistry, for which [illegible] factory "modus operandi" has been [illegible] appearing to result from a combination of [illegible] action and electron emission.

A study of the ultra-violet spectrum of [illegible] allotropes gives us an insight into the various [illegible] actions involved, and quantitative relations [illegible] tained by an application of the quantum the[illegible] time the study of the disintegration of [illegible] molecules by electron emission is as yet in its infancy.

The work of Sir J. J. Thomson at the [illegible] Laboratory on the subject of thermionic [illegible] new vista of electro-chemical research, for it [illegible] that the elements, including oxygen, can exist [illegible] the form of allotropes, but also as allotropic [illegible] possessing electrical charges. It remains for the future to reveal the influence of these charges on chemical [illegible].

Thanks are due to those who have been kind enough to place material dealing with the applications of [illegible] disposal, and if the following pages can arouse [illegible] research both scientific and technical in this, one of the most interesting branches of electro-chemistry, the object of the writer will be fully attained.

ERIC K. RIDEAL.

UNIVERSITY OF ILLINOIS,
ILLINOIS, U.S.A., *14th November*, 1919.

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CHAPTER I.

OZONE.

Early History.

In 1783 Van Marum, a Dutch philosopher, noticed that the air in the neighbourhood of his electrostatic machine (now in the museum at Haarlem, Holland) acquired a marked and characteristic odour when subjected to the passage of a series of electric sparks. Cruickshank in 1801 likewise drew attention to the fact that the oxygen gas produced by the electrolytic decomposition of dilute acids under certain conditions was possessed of a similar odour.

These two investigators merely chronicled the results of their experiments, and did not pursue their inquiries to elucidate the origin of the odoriferous substance. Schönbein, in a memoir presented to the Academy at Munich in 1840, recognised that the smell noted in air subjected to the spark discharge, and in the oxygen generated by electrolysis, was due to the presence of a new gas, to which he gave the name "ozone" (ὄζω—to smell), he also showed that ozone was formed in certain processes of autoxidation, notably by the action of air on phosphorus, but failed to establish the exact nature or composition of this new substance.

We shall have cause to observe, when discussing the processes of autoxidation, the development of Schönbein's hypothesis in that ozone or active oxygen is produced with its

electrical isomer "antozone" by the disruption of the neutral oxygen molecule—

$$O_2 \rightarrow O' \text{ ozone} + \overset{+}{O} \text{ antozone.}$$

This hypothesis naturally led to the division of peroxides into two groups, the ozonides and the antozonides, and to an extended search for the two active electrically charged forms of the oxygen atoms.

Various other speculative hypotheses were made as to the composition of ozone, all unsupported by experimental evidence, thus, Williamson suggested that it might be gaseous hydrogen peroxide, and Baumert considered ozone to be an oxidised form of hydrogen peroxide, i.e. H_2O_3.

Becquerel and Freny first showed that oxygen could be completely transformed into ozone, thus proving that ozone was an allotropic modification of this element.

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These experimenters effected the conversion of oxygen into ozone by the passage of a stream of electric sparks through the gas, the ozone formed being continuously removed by means of a solution of potassium iodide. In this way all the oxygen originally in the tube ultimately disappeared.

Andrews, Tait and Soret ("C.R.," 1876) took up the investigation at this stage, and by the following experiments proved that the allotrope was actually a condensed form of oxygen:—

A tube of volume V connected to a sulphuric acid manometer and containing oxygen gas was submitted to the action of the spark discharge when a contraction in volume v was recorded on the manometer. On heating up the tube to

270° C. the ozone was destroyed and the gaseous mixture then occupied its original volume V.

Soret showed that no change in the volume of the ozonised oxygen (V – v) took place when the gas was exposed to potassium iodide or metallic silver, nevertheless the ozone was destroyed.

When, however, the gas mixture was exposed to turpentine a further contraction in volume was observed, the final

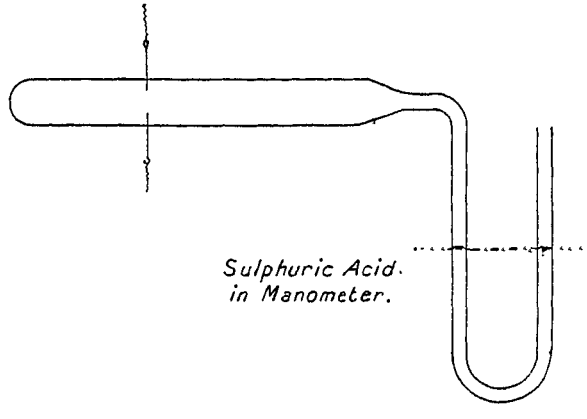

FIG. 1.

volume being V – $3v$ where v was the volume contraction on ozonisation.

As a result of the experiments Soret came to the conclusion that the molecule of ozone consisted of three atoms of oxygen, three volumes combining to give two volumes of ozone—

$$3O_2 = 2O_3,$$

since the volume contraction v on ozonisation is clearly equal to one-third of the oxygen converted into ozone (or one-half of the resulting ozone), which is subsequently absorbed by the turpentine. Further, that when ozone reacted with

potassium iodide or metallic silver it liberated an equal volume of oxygen :—

$$O_3 + 2Ag = Ag_2O + O_2.$$

Soret ascribed the structural formula $\begin{matrix} O—O \\ \diagdown\diagup \\ O \end{matrix}$ to the tri-atomic allotrope of oxygen, and confirmed the existence of ozone by a determination of its density. The theoretical density of ozone at N.T.P. should be equal to one and a half times that of oxygen, and this value was obtained by Soret and Otto by several different methods, which may be briefly described :—

A glass globe of about one litre was filled with pure dry oxygen at a determined temperature and pressure; and subsequently weighed; the oxygen was then displaced by ozonised oxygen reweighed, and the weight of ozone in the flask determined by titration with iodine and sodium thio-sulphate.

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If V be the volume of the globe, containing w grams of oxygen of density Δ, and $w + w'$ be the weight of the ozonised oxygen in the globe, where δ is the density of ozone, and v and w'' the actual volume and weight of ozone in the globe, then

$$\text{(i)} \quad w + w' = \delta v + (V - v)\Delta,$$

$$\text{(ii)} \quad w'' = v\delta,$$

$$\text{(iii)} \quad w = \Delta V.$$

From (i) $$v(\delta - \Delta) = w + w' - \Delta V = w',$$

hence :— $$\delta \frac{w'}{\delta - \Delta} = w''$$

or $$\delta = \Delta\left(\frac{w'}{w'' - w'}\right).$$

From two determinations Otto obtained the value for the ratio $\frac{\delta}{\Delta}$

$$= 1{\cdot}5 - 0{\cdot}0041 \text{ and } 1{\cdot}5 + 0{\cdot}0065,$$

or the density of ozone was practically one and a half time that of oxygen.

Density by Diffusion.

Soret showed that the rate of transpiration through a small aperture of the purest ozone which he could obtain was intermediate between the values obtained for chlorine and carbon dioxide. By applying Graham's law to the numbers obtained for the time of transpiration of ozone and carbon dioxide, taking t' as the time of transpiration for a volume of carbon dioxide of density Δ, and t for an equal volume of ozone of density δ,

$$\text{then } \frac{t'^2}{t^2} = \frac{\Delta}{\delta}$$

the value 1·554 was obtained, taking oxygen as unity. Ladenburg ("Ber.," 1901) at a later date obtained the value 1·3676 for an ozonised oxygen containing 86 per cent. ozone.

We have already referred to Soret's early experiments on the comparison of the volumes occupied by equal weights of oxygen and ozone, in which the ozone formed from a known quantity of oxygen was removed by absorption in turpentine. From the results of seven experiments Soret obtained a mean value differing by only 2·7 per cent. from the theoretical

Physical Properties of Ozone.

Ozone possesses a strong penetrating and characteristic odour which can be detected in concentrations of one part in

a million of air. We may note that there is no unanimity in describing this odour, since it has been likened to sulphur, chlorine and phosphorus (presumably undergoing oxidation when ozone itself would actually be present); other observers have compared it to dilute oxides of nitrogen, whilst De la Coux likens it to lobster.

Dilute ozone is practically colourless, but when viewed through a tube five or six feet long it is found to give a sky blue tint to the column of air.

Hautefeuille and Chappuis ("C.R.," 94, 1249, 1882) obtained liquid ozone by compressing ozonised oxygen to 125 atmospheres at a temperature of – 103° C. Liquid ozone is soluble in liquid oxygen, and Ladenburg ("Ber.," 31, 2508, 1898) obtained a mixture of liquid ozone and oxygen, containing 84·4 per cent. ozone by passing a current of ozonised oxygen through a tube cooled in liquid oxygen, whilst E. Goldstein ("Zeit. Elektrochem.," 50, 972, 1903) obtained pure liquid ozone by immersion of a double walled quartz mercury vapour lamp in liquid oxygen. When a small quantity of oxygen was admitted into the vacuous space it was rapidly ozonised by the ultra-violet light emitted by the mercury vapour and condensed in the form of small drops, the pressure rapidly fell and fresh oxygen could then be admitted. Dewar likewise obtained practically pure liquid ozone by the careful fractionation of liquefied ozonised oxygen. Liquid ozone, which is very liable to explode if accidentally brought into contact with a trace of organic matter or if the temperature be allowed to rise, is a dark blue liquid, opaque in thickness exceeding 2 mm. Olszewski ("Monatsh.," 8, 109, 1887; "Ann. der Physik," 3, 31, 1887) gave the boiling-point

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at – 106° C. to – 109° C., whilst Troost ("C.R.," **126**, 1751, 1898) determined it at – 119° C.

The formation of ozone from oxygen is accompanied by the absorption of heat and the instability of liquid ozone and the gas at ordinary temperatures is doubtless occasioned by its strongly endothermic nature.

$$2O_3 = 3O_2 + 2Q.$$

The lowest value of Q, the heat of decomposition per gram. mol. of ozone, is recorded by Hollman in 1868 as 17,064 calories, later determinations by Berthelot (1876) gave 29,600, Van de Meulen obtained values between 32,600 and 36,000, whilst Remsen gives the highest value of 36,600. The most recent observations of Jahn ("Zeit. Anorg. Chem.," **60**, 357, 1908, and **68**, 250, 1910) give 34,000 (see p. 45).

Ozone is soluble in water, but wide discrepancies are found in the published figures, doubtless occasioned by partial decomposition during solution.

Schöne ("Ber.," **6**, 1224, 1873) obtained the value for the solubility coefficient at 18° C. of 0·366, McLeod at 14° C. 0·2795, Carius ("Ann.," **174**, 30, 1874) at 1° C. 0·834, Ladenburg ("Ber.," **31**, 2510, 1898) gave the solubility at 12° C. as 0·01 per cent. by volume, whilst Mailfert ("C.R.," **119**, 951, 1894) gives the following values for the coefficient :—

Temperature.	*Coefficient of Solubility.*
0° C.	0·64
11·8°	0·5
15°	0·456
19°	0·381
27°	0·27
40°	0·112
55°	0·031
60°	0

about fifteen times the values obtained for oxygen. Mouf-gang ("Woch Brauerei," 28, 434, 1911) determined the following values: 10 mgm. per litre at 2° C. and 1·5 mgm. at 28° C.

In dilute solutions of sulphuric acid (0·03 – 0·09 per cent.) the coefficient of solubility is somewhat higher, as is indicated by the following figures:—

Temperature.	*Coefficient of Solubility.*
30° C.	0·240
38°	0·224
49°	0·156
57°	0·096

Rothmund ("Nernst Festschrift," 391, 1912) has indicated that the above figures are in all probability too low owing to the decomposition of ozone occurring during the estimation of the solubility. He found that this decomposition was remarkably small in 0·1 N. sulphuric acid at 0° C. and obtained a value 0·487 for the absorption coefficient at this temperature; when corrected for the salting out action of the sulphuric acid the coefficient in water would be equal to 0·494.

Ozone is soluble in acetic acid, acetic anhydride, ethyl acetate, chloroform, and carbon tetrachloride (Fischer and Tropsch, "Ber.," 50, 765, 1917), forming blue solutions which are fairly stable. Solutions of ozone in carbon tetrachloride, in which the solubility is seven times that in water, do not undergo decomposition for twenty-four hours.

The decomposition of ozone (see p. 133) is frequently accompanied by a phosphorescence noted by Dewar when passing ozonised air through a capillary opening, and by Otto in the action of ozone on water containing traces of organic matter.

A vivid phosphorescence is likewise obtained when a hot glass rod is brought near the surface of liquid oxygen containing ozone ("Beger. Zeit. Elektrochem.," **16**, 76, 1910).

R. S. Strutt ("Proc. Roy. Soc.," **85**, 10, 1911) has examined a number of cases of phosphorescent combustions, especially marked in vacuum tubes containing ozonised air under low pressures. Phosphorescence was noticed during the oxidation of a number of substances by ozone, amongst the more important being nitric oxide, sulphur, hydrogen sulphide, ethylene, and iodine. The spectroscopic examination revealed a banded spectrum in the majority of cases, but occasionally continuous spectra were obtained.

The spectrum of ozone is exceedingly complex and has been the subject of numerous investigations.

Chappuis ("C.R.," **94**, 858, 1882) found eleven lines lying in the region $\lambda = 628{\cdot}5\ \mu\mu$ and $\lambda = 444\ \mu\mu$ in the visible spectrum, those lying on either side of the sodium lines being particularly distinct and characteristic, $\lambda = 609{\cdot}5 - 595{\cdot}5\ \mu\mu$ and $\lambda = 577$ to $560\ \mu\mu$. Schöne ("Zeit. Anorg. Chem.," **6**, 333, 1894) added two to the above number, whilst Ladenburg and Lehmann ("Ber.," **4**, 125, 1906) noticed a line in the red portion of the spectrum.

J. Stark ("Ann. der Physik," **43**, 2, 319, 1914) has shown that the ozone molecule gives rise to many bands lying between the visible green and the ultra-violet, $\lambda = 210\ \mu\mu$. The bands of long wave lengths were found to be resolvable into line series.

Certain lines attributed to the ozone molecule are frequently caused by other allotropes of the element, either of elementary oxygen in the monatomic or diatomic form, O or

O_2, or of those substances when charged. Thus Stark ("Phys. Zeit.," **14**, 720, 1913) has shown the existence of two distinct arc spectra of oxygen attributable to the substances O_2 and $\dot{O}_2$.

The line in the visible red of the spectrum noticed by Ladenburg and Lehmann (*loc. cit.*) is possibly not due to ozone but to another allotrope of oxygen, viz. oxozone, O_4; whilst the existence of a band in the infra red or thermal region at $\lambda = 1040\ \mu\mu$ has been claimed for ozone but has not received confirmation.

The lines of the oxygen spectrum at the negative electrode of a discharge tube were examined by Schüster, Steubing and F. Croze ("C.R.," **153**, 680, 1916) who gives the following: $\lambda = 685{\cdot}3\ \mu\mu$, 662·5, 603·2, 564·6, 529·6 and 498. Schüster's two negative bands $\lambda = 570 - 584\ \mu\mu$ and $\lambda = 601 - 596\ \mu\mu$ could not be resolved.

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The lines of atomic oxygen O are found in the examination of water vapour as well as in oxygen submitted to intense electrical discharges. Fowler and Brooksbank ("Roy. Astron. Soc.," **77**, 511, 1917) have likewise shown the presence of lines of this series, the third line spectrum of oxygen $\lambda = 559{\cdot}2\ \mu\mu$, and 396·18 in stars of the β type as well as in Wolf Rayet stars.

The ultra-violet spectra of oxygen and its allotropes are of special significance in the consideration of their photochemical interconversion (see p. 70).

That of ozone has been examined by Lenard ("Ann. der Physik," **1**, 480, 1900), Goldstein ("Ber.," **36**, 304, 1903), and more especially Regener ("Ann. der Physik," **20**, 1033, 1906).

The O_2 molecule gives short wave length bands resolvable into lines between the region λ 200 and λ 188 $\mu\mu$ corresponding to the ultra-violet fluorescence of oxygen. Steubing noticed five bands between $\lambda = 183{\cdot}1$, and $191{\cdot}1$ $\mu\mu$, whilst L. and E. Bloch ("C.R.," **158**, 1161, 1914) isolated two new ones conforming to the Delandres formula at $\lambda = 192{\cdot}3$ to $193{\cdot}6$, and $194{\cdot}6$ to $195{\cdot}7$ $\mu\mu$. The ultra-violet oxygen atom O band in the region $\lambda = 230$ $\mu\mu$ and $\lambda = 340$ $\mu\mu$ is observed in the positive column in pure rarified oxygen, and in the decomposition of dissociation of many oxygen-containing compounds. The strongest band (see Meyerheim, Grebe, Holtz and Fowler, "Proc. Roy. Soc.," **94**, 472, 1918) is found at $\lambda = 306{\cdot}4$ $\mu\mu$, and is usually attributed to water vapour.

Investigations on the carriers of positive electricity by Sir J. J. Thomson and his co-workers ("The Carriers of Positive Electricity") have revealed the presence of a great number of allotropes of oxygen which give rise to their respective band spectra. F. Horton ("Phil. Mag.," **22**, 24, 1911) has shown the existence of carriers of positive electricity in oxygen of electric atomic weights, 8, 16, 32, 48 and 96.

Becquerel has shown that the magnetic susceptibility of ozone exceeds that of oxygen, and that the ratio of the specific magnetic susceptibilities exceeds that of the ratio of their densities.

Chemical Properties.

Chemically, ozone is a strong oxidising agent, capable of effecting the oxidation of all the elements with the exception of gold and some of the metals of the platinum group.

It liberates iodine from potassium iodide and brings about

the oxidation of numerous substances such as lead sulphide, manganous salts and ferrocyanides, reactions which form the basis of its qualitative and quantitative detection and estimation.

The general reaction may be expressed by the equation :—

$$M + O_3 = MO + O_2.$$

In some cases, however, oxygen is not liberated, but the whole of the ozone reacts and no free oxygen is evolved. Thus sulphur dioxide is oxidised to sulphuric anhydride by ozone according to the reaction :—

$$3SO_2 + O_3 = 3SO_3$$

(see Brodie, "Phil. Mag.," 1894, and Riesenfeld, "Zeit. Elektrochem.," **17**, 634, 1911). In the combustion of the organic matter in water during the process of sterilisation by ozonised air this reactivity of the ozone molecule as a whole is likewise noted.

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Riesenfeld ("Zeit. Anorg. Chem.," **85**, 217, 1914) observed a similar series of reactions in the action of ozone on sulphur compounds. Three atoms of oxygen in the ozone molecule react with sodium hydrogen sulphite, whilst with neutral sulphites and alkaline thiosulphates only two atoms react, the third being liberated as oxygen gas.

With certain peroxides, such as hydrogen peroxide, it undergoes decomposition as follows :—

$$O_3 + H_2O_2 = H_2O + 2O_2,$$

Rothmund ("Monatsh.," **38**, 295, 1917) showed that the reaction was unimolecular in excess of hydrogen peroxide, but in dilute solutions the ozone underwent catalytic decomposition.

It has found many uses industrially as an oxidising agent, which will be detailed in a subsequent section of this volume. Reference, however, may be made to the deodorising of air, the conversion of manganates into permanganates, of chlorates into perchlorates, and the "drying" of oils in the preparation of linoleum and varnishes.

At suitable temperatures selective oxidation of undesirable substances which give an objectionable colour or odour to many fats and waxes may be obtained, and such processes of bleaching are receiving extended application. Attempts have also been made to accelerate the ageing of spirits and wine by fractional oxidation with ozone.

Ozone is a powerful germicide, as was first indicated by Fröhlich. Its high germicidal activity is doubtless due to its oxidising power, and as a dual agent of this character it has been fairly extensively employed for the sterilisation of public water supplies, for the treatment of wounds in hospitals, and for various purposes of sterilisation and preservation in industries, such as hide preservation, cold meat storage and the like. Although ozone in high concentrations will effect the sterilisation of air, yet such concentrations as are necessary (ca. ·05 per cent.) are not capable of respiration without damage to the tissues, consequently its chief function is as a deodoriser and "freshener" for air in confined and crowded spaces.

In the realm of organic chemistry ozone has received application in two directions, firstly as an oxidising agent of great strength which introduces no foreign matter, and secondly as a reagent for the ethylene linkage $-C=C-$.

As an oxidising agent it is employed for the preparation

of vanillin on an extremely large scale. The production of other substances, such as heliotropine, piperonal, and anisaldehyde, can also be accomplished with its aid (see chap. ix.). Apart from its powerful oxidising properties, ozone will react with certain substances in two definite and characteristic ways to form ozonates and ozonides.

The Ozonates.

Baeyer and Villiger ("Ber.," 35, 3038, 1908) state that strong ozonised air fumes in moist air colours blue litmus red, and causes an increase in the conductivity of distilled water when passed through it. They therefore regarded ozone as the anhydride of an unstable ozonic acid, H_2O_4. According to these authors, if due precautions are taken, highly coloured ozonates may be prepared by the interaction of ozone and moist solid alkali hydroxides or concentrated solutions of the same at low temperatures.

The ozonates are usually orange or brown. If ozone be passed into a cold ammonia solution, it acquires a dark red colour attributed by these investigators to the formation of ammonium ozonate, NH_4HO_4. Lithium ozonate was found to be least, and that salt of caesium most stable.

A white granular precipitate of calcium peroxide is formed on the passage of ozonised air into cold lime water.

According to W. Manchot ("Ber.," 41, 47, 1908), Baeyer and Villiger's results are to be attributed to the presence of small quantities of oxides of nitrogen in their ozonised air, since he found that ozone possessed no acidic quali-

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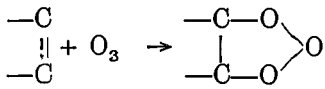
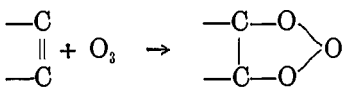
The Ozonides.

The ozonides are formed by the interaction of ozone with organic compounds containing unsaturated ethylene linkages according to the general equation :—

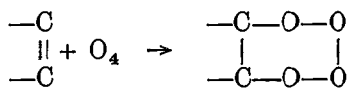


Discovered by Harries ("Ann.," **343**, 311, 1905; "Ber.," **38**, 1195, 1905), this reaction was successfully employed by him to elucidate the composition of rubber (see p. 170), and has of recent years been frequently utilised to identify the presence of ethylene linkages.

Where compounds containing ethylene linkages are treated with strongly ozonised oxygen (ca. 40 per cent. O_3) the ozonides thus formed on analysis yield more oxygen than is to be expected by the assumption of simple saturation of the ethylene linkage according to the equation :—



According to Harries, oxozonides are formed by interaction of the organic compound with oxozone present in the gas :—



More recent experiments, however (see p. 184), have failed to establish the existence of oxozone in ozonised air or oxygen and consequently some other explanation for the formation of oxozonides must be advanced.

CHAPTER II.

THE NATURAL OCCURRENCE OF OZONE.

THE occurrence of ozone in ordinary atmospheric air has long been a matter of dispute. C. Schönbein ("J. f. Prakt. Chemie," **73**, 99, 1858), as early as 1858, showed that starch iodide paper, when exposed to the air, slowly turned blue, thus demonstrating the existence of some oxidising agency. He noted that the rate of liberation of iodine varied from day to day and attributed this to an alteration in the ozone content of the air. Clöez and Bineau pointed out that the liberation of iodine from starch iodide could likewise be caused by the presence of oxides of nitrogen naturally present in atmospheric air.

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Houzeau ("Ann. Chem. Phys." IV, **27**, 5, 1872, and "C.R.," **74**, 712, 1872), as a result of over 4000 determinations with neutral litmus starch iodide paper, came to the conclusion that ozone was present in atmospheric air in addition to the frequent occurrence of oxides of nitrogen. As a maximum ozone content Houzeau recorded 2·8 mgm. per cubic metre. Houzeau's views were supported by Hartley ("Trans. Chem. Soc.," **39**, 10, 111, 1881, and "Nature," **39**, 474, 1889), who noted that many of the dark lines of the solar spectrum were coincident with those that would have been produced on the assumption that atmospheric ozone absorbed light of these particular wave lengths emitted from the sun,

thus exhibiting the Frauenhofer lines; which conclusions were confirmed by Meyer ("Ann. der Physik," IV, **12**, 849, 1903).

The vivid blue colour of ozone was asserted by Hartley to give the characteristic coloration to the summer sky, an alternative theory to the one first propounded by Lord Rayleigh in 1871 (Hon. S. W. Strutt, "Phil. Mag.," **11**, 107, 1871) and extended by Schüster ("Theory of Optics," p. 325) and King ("Trans. Phil. Roy. Soc.," A, **212**, 375, 1913).

Rayleigh showed that the intensity of the light scattered by small particles of dust in the atmosphere would vary inversely as the fourth power of the wave length, i.e. the light in the ultra-violet and blue end of the spectrum being of the shortest wave length would be most intensely scattered and thus made visible. It may be noted that in Lord Rayleigh's experiments the sky light appeared somewhat bluer than anticipated by this theory, and thus indicated that absorption by ozone may be a contributary cause to the colour of the sky. C. Fabry and H. Buisson ("C.R.," **156**, 782, 1913), as a result of a series of experiments on the absorption coefficient of ozone for light of the wave lengths $\lambda = 255\ \mu\mu$ to $330\ \mu\mu$, showed that a thickness of only $25\ \mu$ of ozone reduces the incident light intensity by over 50 per cent. For a wave length of $\lambda = 300\ \mu\mu$ the proportion of transmitted light for a thickness of 5 mm. of ozone was only 1 per cent., approximating to the conditions of the terrestrial atmosphere exposed to solar radiation. If uniformly distributed this would equal ·6 c.c. or 1·4 mgm. per cubic metre; this concentration is somewhat high for air at low altitudes, hence it may be argued that with increasing altitudes the ozone content rises.

E. Kron ("Ann. der Physik," 45, 377, 1914) records λ = 325 $\mu\mu$ as the limit of the effective solar spectrum at sea-level on the clearest days. Fabry and Buisson's results between the wave length λ = 200 and λ = 350 $\mu\mu$ are shown in the following graphical form :—

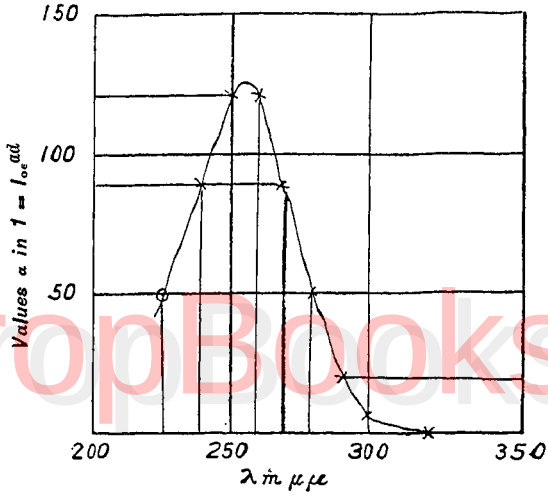

FIG. 2.

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More recently Fowler and Strutt ("Proc. Roy. Soc.," 93, 577, 1917) showed that the Frauenhofer lines between the wave lengths λ = 319·9 $\mu\mu$ and λ = 333·8 $\mu\mu$, the ultra-violet lines shown by Ladenburg and Lehmann to be present in the ozone absorption spectrum, were present in the greatest intensity in the solar spectrum at low altitudes, or when the terrestrial air stratum through which the light had to pass was greatest, thus again supporting Hartley's contention that the atmospheric ozone was an effective agent in fixing the extension of the solar spectrum in the ultra-violet.

Strutt ("Proc. Roy. Soc.," 114, 260, 1918) likewise showed that the limitation of the solar spectrum to the lower wave

length of $\lambda = 294{\cdot}8\ \mu\mu$ was due to the absorption by atmospheric ozone. By long distance experiments on absorption of the light from a cadmium spark and mercury vapour lamp, the lower air, mass for mass, was found more transparent than the upper air, and that if the absorption was not due to dust, the ozone content would not exceed 0·27 mm. at normal pressure, in four miles of air.

Engler and Wild ("Ber.," **29**, 1940, 1896) likewise confirmed the presence of atmospheric ozone by the action of air on manganous chloride paper, whilst Schöne in 1897 ("Brochure," Moscow, 1897) obtained as maxima and minima the following values :—

Maximum, 100 mg. per cubic metre.
Minimum, 10 „ „ „

In the same year, Thierry ("C.R.," **124**, 460, 1897) made the important observation from experiments conducted on Mont Blanc, that the ozone content of the atmosphere rose with increasing altitude, thus, at 1000 metres height he obtained 0·039 mg., and at 3000 metres, 0·094 mg. of ozone per cubic metre of air. Similar figures were observed by H. de Varigny (Smithsonian College, "Proc.," **39**, 27), viz. a maximum and minimum of 0·03 and 0·01 mg. per cubic metre.

These observations were continued by Hatcher and Arny ("J. Amer. Pharm.," **72**, 9, 1900), who determined the amount of ozone in the air by two different methods, viz. the iodide and arsenitic titration processes, as maxima and minima, they observed the following values :—

Method of Estimation.	*Minimum.*	*Maximum.*
Iodide	158	316 mg. per cubic metre.
Arsenite	34	80 „ „ „ „

Henriet and Bonyssy ("C.R.," 146, 977, 1908) showed that the ozone content of the air at ground level varied approximately inversely with the carbon dioxide concentration.

Hayhurst and Pring ("J.C.S.," LXII, 868, 1910) drew attention to the wide variation of the results obtained by numerous investigators, and conducted a series of observations on Glossop Moor in Derbyshire. They showed, utilising Houzeau's original method of estimating both iodine and alkali liberated from potassium iodide solutions, a procedure which was found to give extremely accurate results, both for ozone and mixtures of ozone and nitrogen dioxide, that in this neighbourhood at least, oxides of nitrogen were always present in the air up to an altitude of 8000 ft., and that the quantity of ozone present, if any, was too small to be detected. With an increase in the altitude small quantities of ozone were obtained up to a height of 10 miles. Concentrations of the order of 0·12 to 0·4 mg. per cubic metre of ozone, and smaller quantities of oxides of nitrogen were obtained.

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H. N. Holmes ("J. Amer. Chem. Soc.," 47, 497, 1909) has shown that the maximum amount of ozone is formed in moving areas of air under a high barometric pressure when the conditions are favourable for bringing air of high altitudes close to the earth's surface.

It may be concluded that ozone is a normal constituent of pure air, and that the quantity of ozone in the air increases with the altitude. Seasonal variations in the ozone content have likewise been obtained. Thus, Houzeau, as a result of eight years observation with neutral and alkaline iodide test-papers (*loc. cit.*), noted that the ozone content of the atmos-

phere rose in spring and summer, but sank to very small proportions in autumn and winter. Bérigny observed a maximum in the month of May, and a minimum in November, and gives the following order for decreasing ozone content. May, March, April, June, August, July, September, January, October, February, November.

Pring ("Proc. Roy. Soc.," **96**, 204, 1914) extended his investigations to the air in the high Alps; at 2100 metres, he obtained the value 1·7 mgr. per cubic metre, and at 3580 metres 8·8 mgr. per cubic metre. No considerable increase in the ozone content was observed at altitudes up to 20 km. Oxides of nitrogen and hydrogen peroxide were absent in the air at the higher altitudes.

Usher and Rao ("J. C. S.," **111**, 779, 1917) conducted a series of estimations in India on the ozone (by manganese dioxide), hydrogen peroxide (by chromic acid), and oxides of nitrogen content of the atmosphere. They could not detect the presence of ozone although oxides of nitrogen in concentrations of from 1 to 5 parts per million were frequently obtained.

The ozone concentration in the lower air strata likewise increases during periods of storm or after heavy rain storms, and the south and south west winds are said to be richer in ozone than the northern ones.

R. Nasini ("Atti. d. R. Accad. Lincei," **21**, 740, 1912) records interesting cases of naturally occurring ozonised water; he states that the acid waters of Bagnone, Monte Amiata are highly ionised, and contain 1·25 of oxygen, and 0·135 c.c. of ozone per litre.

Sources of Natural Ozone.

Various alternative hypotheses have been advanced to explain the mode of formation of this small ozone concentration in atmospheric air. It is at once evident that even this minute quantity exceeds the normal thermal equilibrium amount, and consequently there must be a continuous source of ozone. We may classify the various hypotheses as to this source under three groups:—

(*a*) chemical; (*b*) photo-chemical; (*c*) electrical.

Natural Chemical Processes.

The earlier investigators such as Schönbein, Houzeau, Bérigny, Peyrou, and Marié Davy, were of the opinion that the green vegetation of plant life was responsible for the production of ozone, thus accounting for the observed maximum and minimum ozone content in the months of May and November respectively. It was shown, however, that coloured plants yielded no volatile oxidising substances whatever, and more recent experiments have shown that the oxidising agent, which can always be detected in green plant growth, is hydrogen peroxide. According to Priestly and Usher ("Proc. Phys. Soc.," **78**, 3, 38, 1906), the plant chlorophyll serves merely as a light sensitiser to bring about the reaction—

$$3H_2O + CO_2 + \text{light energy} = HCHO + 2H_2O_2,$$

the formaldehyde thus formed is subsequently polymerised to formose (d.l. glucose) by the protoplasm of the cell chloroplast.

The hydrogen peroxide is usually destroyed by one of the numerous enzymes, termed oxidases, present liberating molecular oxygen—

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

(see Bach and Choat, "Arch. d. Sci. Phys. et Nat. Geneva," **17**, 4771, 1909), but many investigators suspect that during the decomposition of the hydrogen peroxide small quantities of ozone may be produced.

The production of ozone by the atmospheric oxidation of various gums and essential oils exuded by trees and plants, such as turpentine, sandal-wood oil, or oil of lavender, has long been suspected, and undoubtedly the rapidity with which starch iodide slips are turned blue in a pine forest is, in some measure, due to the ozone present in the surrounding air, although the formation of hydrogen peroxide under these conditions is without doubt the more important natural process contributing to the freshness of the air.

Photo-chemical Processes.

We shall have occasion to refer to the interesting fact that oxygen is ozonised by exposure to ultra-violet irradiation of wave length $\lambda = 120 - 180\ \mu\mu$ whilst ozonised oxygen is resolved into its original form by light of somewhat longer wave length, viz. $\lambda = 330\ \mu\mu$.

Hartley ("Trans. Chem. Soc.," **39**, 10, 111, 1881) noted the presence of Frauenhofer lines in the visible solar spectrum corresponding to those which would be absorbed by ozone. These conclusions in the visible part of the spectrum were confirmed by Meyer ("Ann. der Physik," IV, **12**, 849, 1903) and extended by C. Fabry and H. Buisson ("C.R.," **156**, 782, 1913) and Fowler and Strutt ("Proc. Roy. Soc.," **93**, 77, 1917) to the ultra-violet portion of the spectrum. Furthermore, all experimental evidence indicates that the

ozone concentration is greatest in the upper portion of the atmosphere, where the intensity of the ultra-violet radiation would naturally be greatest (see also K. Birkeland, "Cairo Soc.," 8, 287, 1916). It would appear that the presence of ozone in atmospheric oxygen is largely due to the synthetic operation of solar radiant energy of short wave length ($\lambda = 120 - 180\ \mu\mu$), whilst the limitations in the amount in the upper parts of the atmosphere is caused by the destructive action of light of longer wave length ($\lambda = 300\ \mu\mu$), a dynamic equilibrium being finally established between the rate of formation and the rate of decay. Near the earth's surface, as we have seen, smaller ozone concentrations are obtained, partly owing to the fact that the light of longer wave length penetrates somewhat further into a dusty atmosphere than that of short wave length, but more especially to the reducing action of easily oxidisable substances both on the earth's surface, and carried to low altitudes by the wind. Country air, according to Houzeau, contains more ozone than that around villages, whilst its presence can rarely be detected in towns. This observer, in fact, records the disappearance of ozone in the air after the passage of a crowd on a public fête day, and its gradual reappearance when the normal conditions had been re-established.

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Electrical Processes.

The increasing attention which during the last few years has been paid to a study of atmospheric ionisation and electrification has not only clearly demonstrated that the potential difference between different parts of the atmosphere and between earth or water and the air may reach extremely high

values during periods of atmospheric disturbances such as electrical storms, but even during periods of fair weather, local potential differences of high magnitude may result.

Evidence for the ozonisation of oxygen during periods of intense electrical discharge, either silent as in the aurora, natural corona, and the remarkable Andes glow occasionally observed in S. America (see "Knoche Meteor. Zeit.," **29**, 329, 1912), or violent as in lightning and the so-called *thunderbolt* or globular discharge, is somewhat conflicting. Undoubtedly oxides of nitrogen are present, since these can always be detected during periods of heavy discharge, and in many cases it appears probable that ozone is formed either without or more probably in conjunction with the oxides of nitrogen.

Thornton ("Phil. Mag.," **21**, 630, 1911) has advanced the view that the globular discharges themselves are purely gaseous bodies and consist of ozone in active combination.

In a subsequent chapter we shall observe that the conditions for the possible ozonisation of oxygen by means of ionisation are established when a discharged electron or a gas ion strikes an oxygen molecule with sufficient violence so as to permit the temporary distortion of, or the actual removal of one of the valency electrons circulating round the oxygen molecule from its orbit, and a rough computation of the voltage of discharge which is necessary to give the emitted electron this requisite energy is but nine volts, a relatively low figure.

The potential difference between strata of air during periods of fine weather is frequently extremely great and quite sufficient to produce atmospheric ionisation, with the consequent possible production of ozone, thus P. Mercanton

("Terrest. Magn.," **22**, 35, 1917) obtained a P.D. of 1,960 volts per metre on the top of a tower at Lui-tsze, 650 metres above sea-level.

C. Chree ("Phil. Trans.," **215**, A, 1915) gives 100 volts per metre as the average potential gradient in the atmosphere at Kew for the last fifteen years.

McLennan ("Nature," **92**, 421, 1913) obtained the following values for the number of pairs of ions formed per second per cubic centimetre of air, nine ions in the air over the land and four over sea water. He ascribed them at first to the influence of the ultra-violet light itself, a view supported by the experiments of G. Simpson ("Monthl. Weather Review," **44**, 115, 1916), who found that at a height of 6000 metres over thirty times as many ions were formed per second as at sea-level. W. Swann ("Terrest. Magn.," **21**, 1916) likewise showed that the upper air was a region of high electrical conductivity, the source being the ultra-violet light of amplitude $\lambda < 135\ \mu\mu$, a fraction only 1 of 10^{-6} of the total radiant energy derived from the sun. The production of ozone by natural ionisation is thus chiefly a secondary effect of ultra-violet irradiation, which, as we have already noted, is one of the chief ozonising agencies in the atmosphere. Natural ionisation and consequent ozonisation is, however, not entirely derived from ultra-violet radiation, since ionisation and small quantities of both ozone and hydrogen peroxide are formed by the evaporation of water in air, especially in the neighbourhood of fountains and waterfalls, where conditions of spray formation obtain.

A. Besson ("C.R.," **153**, 877, 1911) noted that the maximum concentrations of ozone and hydrogen peroxide were

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formed in air during the fall of heavy drops of rain from a previously clear sky in hot summer weather.

C. Oddo ("Gaz. Soc. Chim. Ital.," 45, 395, 1915) ascribes the formation of gas ions under these conditions to the spontaneous ionisation of water vapour when rarified. One kilogram of moist air (773·4 litres when dry at N.T.P.) contains 89×10^{-20} hydrogen and hydroxyl ions at 15° C. and 760 mm. pressure; he shows that a fall in temperature naturally diminishes the content of water vapour in the air but also increases the degree of ionisation below 32° C., where it is practically zero. The optimum temperature range for maximum ionisation was found to be 5° to 20° C., which, it may be noted, is the optimum for animal and vegetable life in the temperate zones.

Lenard, in a series of researches on the Electricity of Waterfalls ("Ann. der Physik," 45, 7, 100, 1914), showed that ionisation was effected not only by the impact of suspended drops upon obstacles such as rocks or stones, but by impact of drops against each other resulting in the production of secondary drops.

CHAPTER III.

CHEMICAL PRODUCTION.

An indication of the production of ozone can be observed in a great variety of chemical reactions such as the decomposition of certain peroxides, in processes of autoxidation, and in many cases of combustion of gaseous fuels. In the latter case the ozone is doubtless of a purely thermal origin and a consideration of the mechanism of production by this means will be deferred to a subsequent section.

Ozone can nearly always be detected in oxygen resulting from chemical decomposition. The temporary existence of atomic oxygen liberated according to the equation :

$$M''O_2 + H_2SO_4 \rightarrow MSO_4 + H_2O + O$$

has not yet been definitely proved, although the evidence for the formation of atomic hydrogen by similar processes is now extremely strong. In any case during the decomposition of the peroxides, the atomic oxygen polymerises with great rapidity to the molecular form:—

$$O + O \rightarrow O_2.$$

C. Brodie ("Phil. Trans.," **141**, 759, 1850) first advanced the view that ordinary oxygen during processes of chemical action was split up into two parts termed ozone and antozone.

$$O_2 \rightarrow O' \text{ (ozone)} + \overset{+}{O} \text{ (antozone)}.$$

As we shall have occasion to note in discussing processes of

autoxidation, Brodie's hypothesis was strongly supported by the experimental work of Schönbein.

R. Clausius ("Zeit. Phys. Chem.," **103**, 644, 1858) suggested that Brodie's so-called "ozone" and "antozone" were identical with atomic oxygen, possessing opposite electric charges

$$O_2 \rightarrow \overset{+}{O} + O'.$$

This view was further enlarged upon by van't Hoff ("Zeit. Phys. Chem.," **16**, 411, 1895), who, as a result of his studies on the autoxidation of phosphorus, came to the conclusion that there exists a definite equilibrium in normal gaseous oxygen between the molecular and atomic form, the atomic being charged :—

$$O_2 \rightleftarrows \overset{+}{O} + O'.$$

Nernst ("Zeit. f. Elektrochem.," **9**, 891, 1903) showed, from a series of observations on the electromotive force of ozone-oxygen cells, that if the three allotropes of oxygen were assumed to exit in equilibrium with each other under normal conditions, according to the reversible equations :—

$$O_3 \rightleftarrows O_2 + O$$
$$O_2 \rightleftarrows O + O,$$

none of the allotropes possessing an electrical charge, then the equilibrium concentration of the atomic oxygen would be only $1/10^{23}$ of the normal ozone concentration, which we shall see is of the order 10^{-5} per cent. The normal concentration of atomic oxygen is, therefore, so small as to render its existence as a chemical substance, to which the ordinary methods of statistical calculation of its concentration and properties in bulk can be applied, extremely doubtful.

Nevertheless, the formation of ozone in small quantities may be expected to occur in the decomposition of the peroxides, since, on the above assumption, the following sequence of chemical reactions may be assumed to occur :—

(i) $BaO_2 \rightarrow BaO + O$.

(ii) $O + O \rightarrow O_2$.

(iii) $O_2 + O \rightarrow O_3$.

We have already noted that reaction (ii) proceeds with great rapidity, and that reaction (iii) is merely a side reaction, which will only proceed during the evolution of oxygen. Any ozone formed may, of course, be subsequently decomposed by catalysis at the surface of the decomposed peroxide, or by the somewhat elevated temperature necessary to cause decomposition of the peroxide.

Houzeau, in fact, was able to obtain concentrations as high as 28 gms. of ozone per cubic metre of oxygen evolved, by gently heating small quantities of powdered barium peroxide in eight times its volume of concentrated sulphuric acid. Hydrogen peroxide is likewise formed in small quantities under these conditions :—

$4H_2SO_4 + 4BaO_2 \rightarrow$ (i) $4BaSO_4 + 4H_2O + 2O_2$

(ii) $4BaSO_4 + 4H_2O + O_3 + O$

(iii) $4BaSO_4 + 4H_2O_2$.

The same investigator showed that similar results were obtained with other peroxides, notably those of magnesium, zinc, sodium, and potassium.

Even better results can be obtained by the decomposition and gentle dehydration of permanganic acid or potassium dichromate,

$$Mn_2O_7 \rightarrow 2MnO_2 + O_3.$$

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As dehydrating agent, sulphuric acid is most conveniently employed in the proportions of one of potassium permanganate to two of sulphuric acid. De la Coux ("L'Ozone," p. 67) states that oxalic acid can be likewise employed in the proportion of 10 gms. of permanganate to 15 gms. of oxalic acid, and that 90 c.c. of oxygen containing 3 mgm. of ozone can be obtained from this mixture.

Satisfactory yields of ozone may also be obtained by the cautious addition of barium peroxide to a solution of potassium permanganate in sulphuric acid, of density 1·85.

By the thermal decomposition of the persulphates, small quantities of ozone are likewise disengaged, Malaquin ("J. Pharm. Chem.," VII, 3, 329, 1911) gives the following details for the preparation of ozonised oxygen by this means. Twenty gms. of dry and freshly prepared ammonium persulphate are mixed with 15 gms. of nitric acid in a small flask; the air is subsequently displaced by carbon dioxide, and the mixture cautiously raised to 65° to 70° C. The reaction, which is strongly exothermic, proceeds somewhat vigorously when once started, and the resulting oxygen, after removal of the carbon dioxide, contains 3 to 5 per cent. of ozone and small quantities of nitrogen.

Moissan, in his researches on the properties of fluorine, which he isolated by the electrolysis of fused potassium hydrogen fluoride, noted that appreciable quantities of ozone were produced when a few drops of water were introduced into an atmosphere of fluorine.

The formation of ozone proceeding according to the equation :—

$$3F_2 + 3H_2O = 6HF + O_3,$$

is especially marked at low temperatures, when the rate of thermal decomposition of any ozone formed is considerably reduced.

An ozone content of upwards of 14 per cent. in the oxygen disengaged by means of this reaction may be obtained, if the temperature be maintained at 0° C. De la Coux ("L'Ozone," p. 70) suggests that the preparation of strongly ozonised oxygen, by this method, offers some hope of technical application.

Small quantities of ozone may likewise be obtained by the thermal decomposition of other oxygen-containing salts, but the quantity of ozone in the liberated oxygen is far smaller than in the cases alluded to above. Thus Rammelsberg noted that ozone may be detected in the oxygen evolved, on heating crystallised periodic acid up to 135° C.

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Periodic acid is formed by the action of iodine on an aqueous solution of perchloric acid, and can be obtained as crystals containing two molecules of water. When heated carefully, periodic anhydride is formed.

$$2(HIO_4 . 2H_2O) \rightarrow I_2O_7 + 5H_2O,$$

which on continued heating, loses oxygen to form iodic anhydride:—

$$I_2O_7 \rightarrow I_2O_5 + O_2.$$

The iodic anhydride itself suffers decomposition into its elements at 300° C., consequently the liberation of ozonised oxygen by decomposition of the crystallised periodic acid only takes place within a somewhat narrow temperature range. Aqueous solutions of the acid and its sodium salt likewise gradually acquire the smell of ozone.

O. Brunck has shown that commercial samples of potassium chlorate liberate ozonised oxygen during thermal decomposition, although purified samples fail to yield any ozone. The yield of ozone is sensibly increased by the addition of manganese dioxide, thus equal weights of manganese dioxide and potassium chlorate liberate 0·3 per cent. of the weight of chlorate employed in the form of ozone. With twenty-five times as much manganese dioxide, over 1·5 per cent. of the weight of chlorate can be recovered in this form. Other oxides, such as those of copper, iron and zinc do not exhibit this behaviour, which appears to be characteristic of manganese dioxide, although slight activity is noted in the cases of the oxides of nickel and cobalt. This is doubtless associated with the property of forming unstable peroxides, which undergo secondary decomposition, liberating atomic oxygen, which can secondarily react with the molecular form to produce ozone.

In the thermal decomposition of many metallic peroxides the presence of ozone may be detected in the oxygen evolved, the yield of ozone being naturally greater in the case of those peroxides which undergo thermal decomposition at relatively low temperatures, such as silver oxide, yielding oxygen containing 4 to 5 per cent. of ozone. Lead peroxide and mercuric oxide are likewise capable of yielding small quantities of ozone.

If the peroxide of manganese, or cobalt, or nickelic oxide be subjected to thermal decomposition in a current of oxygen, appreciable quantities of ozone are stated to be formed.

All these oxide decompositions, resulting in the formation of small quantities of ozone, may be referred to chemical

processes of activating atmospheric oxygen, whilst in the case of the decomposition of chlorates and iodic anhydride these salts may be regarded as convenient sources of oxygen.

In the case of the elements of the first group of the periodic table, namely, copper, silver and gold, the sub and normal oxides of copper, Cu_4O, Cu_2O, and CuO, are somewhat too stable, cupric oxide possessing only a small dissociation pressure at very high temperatures. The oxides of both silver and gold, on the other hand, dissociate much more readily, silver oxide possessing a dissociation pressure equal to that of atmospheric oxygen at 250° C. Silver peroxide, Ag_2O_2, readily liberates hydrogen peroxide and oxygen containing ozone when dissolved in acids. Mercuric oxide closely resembles silver oxide in its chemical properties.

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The general reactions involved may be expressed by the following sequence of reactions :—

(i) $2M + O_2 = 2MO$;

(ii) $2MO = 2M + 2O$;

(iii) $2O \rightleftarrows O_2$;

(iv) $O + O_2 \rightarrow O_3$;

in which by the operation of the first two reactions the oxygen molecule is temporarily split up into its atoms, the necessary energy to perform this operation being supplied by heating or cooling the metal to form or decompose the oxide. The atomic oxygen so formed may then instantaneously recombine to form molecular oxygen or combine with molecular oxygen to form ozone.

Ozone Production by Autoxidation.

It had long been known that many substances when exposed to the air undergo a process of slow oxidation.

Exemplifications are found amongst the most diverse types of substances such as the corrosion or rusting of metals, e.g. zinc, lead and iron, of certain non-metallic elements such as sulphur and more especially phosphorus, and in many organic substances, such as benzaldehyde, turpentine, linseed oil and various essential oils, such as oil of cinnamon, lavender or citronella.

It was formerly thought that these reactions were comparable to the ordinary processes of oxidation or combustion except in so far as the reaction velocity was exceedingly low. In 1858, however, C. F. Schönbein ("J. f. Prakt. Chemie," **73**, 99, 1858, *et seq.*, to 1868) opened a new and interesting chapter in the theory of oxidation by showing that in these cases of slow oxidation, for every molecule of oxygen consumed by the substance undergoing oxidation a molecule of oxygen was simultaneously transformed to a more active state. This activated oxygen would then secondarily react to form a fresh series of new substances.

Thus in the presence of oxygen, ozone could be produced; in the presence of water as in the wet oxidation of the metals, an amount of hydrogen peroxide was produced equivalent to the quantity of metal oxidised. In the presence of other oxidisable substances the active oxygen can oxidise them, frequently bringing about oxidations which cannot be accomplished by ordinary atmospheric oxygen; thus indigo is converted into isatin during the autoxidation of palladium hydride or benzaldehyde.

The quantitative relationship between the production of active oxygen and the quantity of substance undergoing the process of slow oxidation was shown by Schönbein to hold in

the case of the wet oxidation of the metal by saturation of the quantity of hydrogen peroxide and oxygen produced.

An interesting confirmation of Scheiber's views was afforded by A. Genthe's investigation on the drying of linseed oils ("Zeit. Angew. Chem.," 19, 201, 1906). It had been previously shown by Lippert ("Zeit. Angew. Chem.," 11, 412, 1898) and Weger ("Chem. Rev. Fett- u. Harz," 4, 345, 1899) that the drying of linseed oil was virtually

a process of atmospheric oxidation. Genthe examined the reaction velocity of the process of oxidation and found that the time-increase of weight curves for the drying of a thin film of linseed oil exhibited the common character of an autocatalytic reaction.

It will be observed that the initial rate of drying increases somewhat slowly with the time, as, however, the quantity of autocatalyst increases simultaneously the reaction proceeds at an ever-increasing velocity and only begins to sink when

the quantity of oil remaining to be oxidised diminishes in amount.

It had therefore to be assumed that in the process of drying, a catalyst was simultaneously formed, thus if a and b be the initial concentrations of the linseed oil and catalyst, then the rate of oxidation of the oil after a time t will be given by the equation: –

$$\frac{dx}{dt} = K(a - x)(b + x).$$

Genthe, in fact, showed by his experiments on reaction velocity that there was a quantitative relationship between the quantity of linseed oil oxidised and the quantity of autocatalyst simultaneously produced.

Houzeau (1860), Genthe (*loc. cit.*), Hazura ("Zeit. Angew. Chem.," 1, 312, 1888), Kissling ("Zeit Angew. Chem.," 4, 395, 1891) and Friend ("Proc. Paint and Varnish Soc.," 1914) all showed that the autocatalyst was an unstable peroxide, since it liberated iodine from potassium iodide and showed the other reactions of a peroxide and a similar catalytic acceleration could be produced by the addition of ozone, benzoyl peroxide, oxidised turpentine or ether, to the linseed oil. It is still a matter of uncertainty as to the nature of this catalytic peroxide. Houzeau was of the opinion that it was dissolved ozone, whilst other investigators support the theory of an unstable peroxide of linoleic acid, similar in character to benzoyl peroxide. It appears probable that small quantities of ozone can be isolated from turpentine, oil of cinnamon and other essential oils, undergoing atmospheric oxidation, but that most of the activated oxygen is absorbed or combines with part of the substance to form a peroxide.

Jorrisen and Reicher ("Ber.," **30**, 1451, 1897; "Zeit. Angew. Chem.," **22**, 6829, and "Chem. Zeit.," **26**, 99, 1902) showed that ozone could be formed during the reduction of certain oxidising acids, such as chromic acid, attributed to the intermediary formation of an unstable peroxide with its subsequent decomposition:

$$CrO_3 + (COOH)_2 \rightarrow H_2O + \begin{matrix} O & & O & O-C \\ & Cr & & | \\ O & & O & O-C \end{matrix}$$

Relatively large quantities of ozone, however, are produced in the autoxidation of phosphorus, and in view of the conveniences of this method of preparation the following details may be given: A rapid current of air is passed through a bottle containing sticks of yellow phosphorus, moistened with a dilute sulphuric acid acidified solution of potassium permanganate or bichromate. The reaction proceeds but slowly at 6° C., whilst the optimum temperature is stated to be 24° C. Under reduced pressure the reaction still proceeds at 0° C. As is well known, pure oxygen reacts but slowly with phosphorus except under reduced pressure. A 20 per cent mixture of oxygen in hydrogen is particularly efficacious for the production of ozone, but the phosphorus is liable to become extremely hot, with the attendant risk of explosion. Small quantities of hydrogen peroxide are simultaneously produced. From time to time the stale phosphorus should be re-fused in order to remove the superficial layer of phosphoric acid which causes a diminution in its activity.

We have already noted that the theory of Brodie, developed by Clausius and van't Hoff, postulating the existence of two forms of oxygen:—

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$$O_2 \begin{cases} \nearrow \dot{\bar{O}} \text{ (ozone)}, \\ + \\ \searrow \ddot{O} \text{ (antozone)}, \end{cases}$$

was supported by Schönbein as a result of these researches. According to this hypothesis all processes of autoxidation are dual in character, since two substances must simultaneously undergo oxidation. Engler ("Kritische Stüdien über die Autoxydationsvorgänge, Braunschweig," 1903) has attempted to distinguish between these by terming the substance undergoing oxidation the autoxidiser, and the substance simultaneously oxidised the acceptor. Clearly, either the ozonic or antozonic form of active oxygen may react with the autoxidiser or the acceptor to produce "ozonides" or "antozonides"; thus ozone is an "ozonide," and phosphoric acid the "antozonide" produced in the autoxidation of phosphorus. Van't Hoff (*loc. cit.*) noted that the presence of excess of "ozonide" prevented the formation of the antozonide, and thus it necessarily followed that the primary reaction, $O_2 \rightleftarrows \dot{\bar{O}} + \ddot{O}$ was reversible in character. Since the antozonide, viz. phosphoric acid, is not volatile the escaping ozonic form of active oxygen or ozone should be electrically charged. A search for this electrically charged form of oxygen in air which has been passed over phosphorus has yielded conflicting results. Elster and Geitel ("Phys. Zeit.," 16, 321, 1890; "Wied. Ann.," 39, 457, 1903) noted that air thus treated was electrically conducting (see also Matteuci, "Enc. Brit.," VIII, 622, 1855; Naccari, "Atti. della Scienze de Torino," XXV, p. 252; J. Joubert, "Thèse sur la Phosphorescence du Phosphore," 1874; T. Evan, "Phil. Mag.," 5, 38, 512, 1897; J. Chappuis, "Bull. Soc. Chem.," 2, 35, 419, 1881).

However, Gockel ("Phys. Zeit.," IV., 1903) showed that this conductivity was not due to the presence of ozone which could be absorbed without destroying the conductivity.

Barus ("Washington," 1901), Harms ("Phys. Zeit.," IV, III, 1902), and Bloch ("Ann. de Chemie et de Phys.," 11, 25, 1905) likewise showed that the conductivity was not due to the presence of ozone oxygen or charged ozone oxygen, but to oxides of phosphorus collected round charged nuclei, forming aggregates of fairly large dimensions ($r = 10^{-6}$ cm.), while the actual number of charged gas ions observed fell far short of the stoichiometric ratio, oxygen absorbed : oxygen activated : 1 : 1, as postulated by the hypothesis. A. Blanc ("C.R.," 95, 2, 1170, 1911) showed the existence of both positive and negative ions, the production of which was accompanied by the formation of white fumes. The production of these gas ions was accelerated by allowing the process of oxidation to take place in an electric field.

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K. Przibram ("Akad. Wiss. Wien., Ber.," 120, 247, 1912) showed that the charge on each gas ion was approximately 6×10^{-10} E.S. units, and that $1{\cdot}43 \times 10^{-8}$ gms. of phosphorus in the form of phosphoric acid was associated with each E.S. unit, and $1{\cdot}3 \times 10^{-18}$ gms. of phosphorus in each particle. A. Blanc ("C.R.," 158, 1492, 1911) claims to have discovered the existence of a radiation emitted during the autoxidation of phosphorus like γ rays, extremely soft and not corpuscular in character. They are easily absorbed by air. F. Hoppe Segler ("Zeit. Physiol. Chem.," 2, 23, 1878), and Baumann, adopted the same hypothesis as Schonbein, but substituted the somewhat less confusing term of "nascent" oxygen for Schönbein's "ozone" and "antozone". It is, however,

evident that the case for the existence of charged ions of atomic oxygen of opposite electric sign is not strongly supported by the investigators cited above, although, as we have observed, the existence of uncharged atomic oxygen is a plausible hypothesis.

M. Traube ("Ber.," **15**, 663, 1882, and 1471, 1843; "Gesammelte Abhandlungen," Berlin, 1899), A. Bach ("C.R.," **126**, 2057, 1897), and C. Engler and V. Wild ("Ber.," **30**, 1667, 1897), and others, on the other hand, developed the theory of an intermediate compound.

Thus, according to Traube, the presence of water is necessary for all these processes of slow combustion, a point of view strongly supported by the researches of Mrs. Fulhame ("An Essay on Combustion," London, 1794), B. Baker, H. B. Dixon ("Phil. Trans.," **175**, 630, 315, 4795, 1896), and H. E. Armstrong (B.A. Reports, "Proc. Roy. Soc.," **40**, 287, 1886); the primary reaction taking place is the formation of an oxide and hydrogen peroxide according to the equation :—

$$M + O_2 + H_2O = MO + H_2O_2.$$

The formation of Schönbein's ozonides must thus be considered as due to secondary reactions between the hydrogen peroxide and the acceptor, in some cases exceedingly improbable reactions. Thus, it is difficult to imagine the formation of ozone by the action of oxygen in a dilute solution of hydrogen peroxide according to the following equations :—

$$P_2 + O_2 + H_2O = P_2O + H_2O_2$$
$$H_2O_2 + O_2 = H_2O + O_3,$$

although it is stated that by the distillation of strong solutions of hydrogen peroxide in vacuo ozone can be obtained.

Bach's modification of the hypothesis embodied the conception of the formation of an unstable intermediary peroxide prior to decomposition into an oxide with simultaneous oxidation of the acceptor thus:—

$$M + O_2 \rightarrow M\begin{matrix}O\\ \\O\end{matrix}$$

$$M\begin{matrix}O\\ \\O\end{matrix} + A \rightarrow MO + AO$$

Engler and Wild ("Ber.," 30, 1669, 1897), and Ostwald ("Zeit. Phys. Chem.," 30, 250, 1900) applied Bach's conception of the mechanism of processes of autoxidation to the case under consideration, i.e. the formation of ozone by the autoxidation of phosphorus.

Engler and Wild suggested the following sequence of reactions:

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$$2P + O_2 = P_2\begin{matrix}O\\ \\O\end{matrix}$$

$$P_2\begin{matrix}O\\ \\O\end{matrix} + O_2 = P_2O + O_3.$$

whilst Ostwald suggested that a still higher oxidation form of phosphorus was produced as an unstable intermediate product:—

$$2P + 2O_2 = \begin{matrix}P\begin{matrix}O\\ \\O\end{matrix}\\ \\P\begin{matrix}O\\ \\O\end{matrix}\end{matrix} \rightarrow P_2O + O_3,$$

thus giving the stoichiometric ratio, $P : O_3 :: 2 : 1$ which was actually obtained by van't Hoff.

The fundamental difficulty inherent in the peroxide theory was raised many years ago in a remarkable essay by G. Liveing ("Chemical Equilibrium, the Result of the Dissipation of Energy," Cambridge, 1885). It is evident that the peroxide formed must be endowed with available energy greater than that possessed by atmospheric oxygen, and it is thus difficult to explain its formation as the result of an exothermic reaction from phosphorus and air. It is usually assumed that the chemical energy of one system is not available for another totally different system, i.e. that the energy liberated during the oxidation of phosphorus is dissipated through the system in the form of heat. Liveing introduced the interesting hypothesis, that in certain cases, the liberated energy was not dissipated in this form, but stored up in one, or at least a very few, neighbouring molecules, which would thus be endowed with a great deal of energy. Thus we can imagine a simple transfer of energy from one set of reacting molecules to another set, molecule to molecule, and thus explain the simultaneous equivalent formation of an endothermic compound, during a strongly exothermic reaction.

CHAPTER IV.

THERMAL PRODUCTION

SINCE the formation of ozone is a strongly endothermic reaction, we would expect, as pointed out by Nernst ("Zeit. Elektrochem.," 9, 891, 1903), that the equilibrium

$$3O_2 \rightleftarrows 2O_3$$

would shift over from left to right with elevation of the temperature. An approximate idea of the ozone concentration in equilibrium with oxygen at various temperatures, can be obtained by two independent methods, from a calculation of the value of K, the equilibrium constant by means of the Nernst heat theorem, as well as from the observed measurements of the electromotive force of the ozone, oxygen cell

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According to the Nernst heat theorem ("Applications of Thermodynamics to Chemistry," Silliman Lectures, 1906), Grinnesen ("Ann. Phys.," 26, 401, 1912), Polhitzer ("Berechnung Chemischer Affinitaten nach dem Nernstchen Warmetheorem. Ahrens Sammlung Encke," 1912), a simple expression for the equilibrium constant K, in homogeneous gas, reactions can be obtained in terms of known quantities, provided two basic assumptions are made, firstly, that the entropy of a condensed chemically homogeneous system vanishes at the absolute zero, and secondly, that the specific molecular heat of a gas can be approximately evaluated from a simple expression

$$C_p = 3{\cdot}5 + 2\beta T,$$

where C_p is the molecular specific heat and β a constant. Making these two assumptions (and much experimental evidence has been adduced to prove the validity of the Nernst heat theorem), it is easily shown (*loc. cit.*) that the equilibrium constant can be obtained from the following equation :—

$$\log_{10}K = \frac{Q}{4{\cdot}571T} + 1{\cdot}75\ \Sigma\nu \log T - \Sigma\nu \frac{\beta T}{4{\cdot}571} + \Sigma\nu C,$$

where Q is the heat of reaction,

and $$\nu_a a + \nu_b b = \nu_c c + \nu_d d$$

$$\nu = \nu_a + \nu_b - \nu_c - \nu_d,$$

ν_a, ν_b, ν_c, ν_d being the number of molecules of such species, a, b, c, d, reacting, C_a, C_b, C_c, C_d being the so-called chemical constants of each element or compound reacting,

and $$\beta = \frac{\Sigma\nu C_p - 3{\cdot}5\nu}{2T},$$

applying this equation to the case under consideration, viz. :—

$$2O_3 = 3O_2 + 68{,}000 \text{ calories.}$$

$$\Sigma\nu = [2] - [3] = -1.$$

$$\Sigma\nu c = (2 \times 3) - (3 \times 2{\cdot}8) = -2{\cdot}4.$$

Information as to the specific heat of ozone is at present not available, but with Pollitzer, we may assume that its value is not very different from that of the other triatomic gases, such as sulphur dioxide, which has a molecular specific heat of 10·5, then

$$\Sigma\nu\beta = -\frac{(3 \times 7{\cdot}2) + (2 \times 10{\cdot}5) + 3{\cdot}5}{2 \times 300} = 0{\cdot}005.$$

Hence

$$\log K_p = -\frac{68{,}000}{4{\cdot}571T} - 1{\cdot}75 \log T + \frac{0{\cdot}005T}{4{\cdot}571} - 2{\cdot}4.$$

If x be the fraction of oxygen converted into ozone at equilibrium, then since :—

$$K_p = \frac{p^2O_3}{p^3O_2} = \frac{x^2}{p}$$

when x is small, and p is the total gas pressure,

$$\log x = -\frac{32{,}000}{4{\cdot}571T} - 0{\cdot}875 \log T + 0{\cdot}0005T - 1{\cdot}2 + \tfrac{1}{2} \log p,$$

from this equation the values of x, and thus the percentage of ozone present in oxygen at equilibrium at various temperatures, can be calculated thus :—

T° centigrade.	$P = 1$ $100x$	P = 10,000 atmospheres.
1000°	10^{-8}	10^{-6}
2000°	10^{-5}	10^{-3}
3000°	10^{-3}	10^{-1}

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It will be noted that increase of pressure greatly favours high equilibrium amounts of ozone.

Somewhat higher values for the equilibrium amounts at various temperatures are arrived at by means of evaluating the magnitude of the potential difference between the ozone and oxygen electrode (see p. 63).

The potential difference between two platinum electrodes immersed in the same electrolyte, one saturated with oxygen under a pressure π, and the other with ozone at the same temperature and pressure π_1, is given by the equation :—

$$V = V_o - \frac{RT}{2F} \log \frac{\pi}{\pi_1},$$

where V_o represents the value observed of the potential difference O_2/O_3, at one atmosphere, under conditions of reversibility.

There exists considerable uncertainty as to the values of V_o, thus Luther and Inglis ("Zeit. Phys. Chem.," **43**, 203, 1903) obtained the value $V_o = -0{\cdot}736$ volts; Nernst ("Zeit. Elektrochem.," **9**, 891, 1903), $V_o = -0{\cdot}57$; Fischer and Brauner ("Ber.," **39**, 3631, 1906) $-0{\cdot}64$, and $-0{\cdot}46$ volts.

Calculation from the value of K obtained by the Nernst heat theorem as follows, yields the value $-0{\cdot}83$ volts:—

$$\log K_p = -\frac{68{,}000}{4{\cdot}571T} - 1{\cdot}75 \log T + \frac{0{\cdot}005T}{4{\cdot}571} - 2{\cdot}4.$$

$$\therefore E_{2,1} = \frac{273 \times 4{\cdot}571}{4 \times 23{,}046} 2\left[\left(+\frac{34{,}000}{4{\cdot}571T} + 0{\cdot}875 \log T - 0{\cdot}0005T + 1{\cdot}2\right)\right] = -0{\cdot}83 \text{ volts.}$$

It is evident that if the pressures of oxygen and ozone are so adjusted that the cell shall have zero E.M.F., this will represent the equilibrium conditions between oxygen and ozone.

or $$V_o = \frac{RT}{2F} \log \frac{\pi}{\pi_1},$$

or $$\log \frac{\pi}{\pi_1} = \frac{A}{T}$$

where A is a constant $$= \frac{2FV_o}{R}.$$

The values of the percentage of ozone in equilibrium with oxygen under one atmosphere pressure at various temperatures, as calculated from the above equation for the two extreme values of V_o, i.e. $V_o = -0{\cdot}83$ volts and $V_o = -0{\cdot}46$ volts, are given in the following columns:—

Percentage of Ozone.	*Equilibrium Temperature.* K_c 0·83 volt.	*Percentage of Ozone.*	*Equilibrium Temperature.* K_c 0·90 volt.
10	7900	10	1100°
1	3950°	1	2700
0·1	2630°	0·1	1160°
0·01	1970°	0·01	1100
0·001	1580°	0·001	1040

It will be noted that in this calculation the change in specific heats of the gases with alteration in the temperature have been neglected, consequently the values are probably somewhat too high, and in view of the wide discrepancies between the two values an experimental redetermination of the oxygen ozone electromotive force would be very desirable.

From the foregoing considerations we must conclude that the quantity of ozone in equilibrium with atmospheric oxygen at normal temperature and pressures is scarcely detectable, and that if present in measurable concentrations under these conditions true equilibrium does not obtain. Further appreciable quantities of ozone may be formed at high temperatures and should be capable of detection and estimation.

The estimation of ozone in gases which have been heated up to a high temperature, is somewhat difficult owing to the fact that ozone rapidly undergoes decomposition to its equilibrium concentration during the cooling of the gas mixture. Dewar ("Year Book R.I.," **559**, 1887) inferred that ozone had two centres of stability, one above the melting-point of platinum and the other at ordinary temperatures, whilst between these temperatures ozone is decomposed. Chapman and Jones ("Trans. Chem. Soc.," **97**, 2463, 1913, and **99**, 1811, 1911) showed that at 100 C. nearly 75 per cent. of

the ozone in excess of the almost undetectable equilibrium amount is destroyed in half an hour, whilst at 300° C. it is practically instantaneous.

The explanation of these observations of Dewar is that the velocity of decomposition of ozone from high temperatures down to 100° C. is extremely rapid, whilst below 100° C. the velocity of decomposition becomes markedly slower and the ozone appears to be stable on account of the extremely low velocity of decomposition, the equilibrium being "frozen".

The earlier experiments of Schönbein (Engler, "Hist. Kritic Studien über Ozon," Halle, 1879), Böttger ("Ann. der. Chem.," **125**, 34, 1861), Pincus ("Pogg. Ann.," **144**, 480, 1871), Struve ("Jahresber. f. Chem.," **199**, 1870), and Traube ("Ber.," **18**, 1894, 1885), all indicated that small quantities of ozone were formed during the combustion of hydrogen. Similar results were obtained by the combustion of coal gas, notably by Than ("Jour. f. Prakt. Chem.," **2**, 1415, 1870), Loew ("Zeit. f. Chem.," **65**, 1870), Hosvay ("Bull. Soc. Chem.," **3**, 2, 360, 1881), whilst Zenghilis demonstrated the presence of ozone ("Zeit. Phys. Chem.," **46**, 1903) in the oxygen which had been raised to a high temperature by the combustion of aluminium powder.

Contemporary with these investigations, others were carried out on the synthesis of ozone by merely heating air or oxygen by means of an independent source of heat, as the objection may be raised to the former experiments that the ozone may have been formed by chemical activity (see Ch. III).

As catalytic agent hot platinum or silver was generally employed, notably by V. der Willigen ("Pogg. Ann.," **98**, 511, 1831), Meissner ("Neue Untersuchungen über Elekt.

Sauerstoff," Gottingen, 1863), Leroux ("C.R.," 50, 691, 1860), Troost and Hautefeuille ("C.R.," 84, 946, 1877), Helmholtz ("Wied. Ann.," 32, 18, 1887), and Elster and Geitel ("Wied. Ann.," 39, 912, 1890). Troost and Hautefeuille (*loc. cit.*) detected the presence of ozone in oxygen which had been heated up to only 1400° C. The oxygen was heated by passage through a porcelain tube maintained at 1400° C. In order to effect the rapid cooling of the gas a water-cooled silver tube passed along the axis of the porcelain tube. Samples of oxygen were drawn from the annular space between the porcelain and the silver tubes by aspiration through a small side tube which passed into the silver tube itself.

J. Clements, at Nernst's instigation in 1904 ("Ann. Phys.," 14, 334, 1904), reviewed the whole subject and came to the conclusion that many of the previous observers had mistaken oxides of nitrogen or hydrogen peroxide for ozone. By the use of Arnold and Mentzel's tetramethyl base paper ("Ber.," 35, 1324, and 2902, 1902), which is diagnostic for ozone, Clements showed that ozone could be detected in the hot gases from a Bunsen burner, but only in very small quantities. (Tetramethyl base paper is stated to be sensitive to 0·001 per cent. ozone.)

By the passage of ozonised air containing 1 per cent. of ozone over a glowing Nernst filament maintained at 1000° C. at various speeds up to 80 cms. per second, he showed that the rate of decomposition of ozone was extremely rapid, 1 per cent. O_3 sinking to 0·001 per cent. in 0·007 seconds.

In passing air over a Nernst glower even when heated up to 3000° C., only oxides of nitrogen were obtained, a result which was confirmed by Rossi ("Gaz. Chim. Ital.," 35, 1, 89,

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1905). Clements, however, confirmed the formation of ozone by spark discharge, and Brode ("Zeit. f. Elektrochem.," **11**, 754, 1905) observed the formation of ozone in the high voltage arc at 4000° C. Ozone formation in these latter cases may, however, be attributed to the action of ultra-violet light (see p. 79) or electrical ionisation, and not to the result of the establishment of a purely thermal equilibrium.

Fischer and his co-workers Brauner ("Ber.," **39**, 940, 1906), Marx ("Ber.," **39**, 3631, 1906, **40**, 443, 1907), and Wolf ("Ber.," **44**, 2956, 1911) realised from Troost and Hautefeuille and Clements' experiments that rapid cooling was essential to preserve any ozone which might be formed, from secondary thermal decomposition, during the process of cooling to the point where the reaction of decomposition was negligibly small. They showed by a series of interesting researches that ozone could be formed by thermal methods provided that the right conditions were obtained.

It was shown that ozone could be produced by plunging a jet of burning hydrogen or acetylene into liquid air, the ozone formed by the local heating being thus preserved by rapid cooling.

When liquid oxygen was substituted for liquid air, large quantities of ozone were formed and the liquid rapidly became dark blue in colour, similar to ammoniacal solutions of copper salts. When an electrically heated platinised wire was immersed in liquid oxygen, practically no ozone was formed. This somewhat unexpected result was shown to be due to the fact that the platinum wire in the liquid oxygen underwent dispersion into colloidal particles which catalytically accelerated the decomposition of the ozone. A bright

platinum wire, protected from dispersion by a coating of the oxides of zirconium and yttrium, gave a uniform yield of ozone. Using a glowing Nernst filament in liquid air and oxygen, ozone was produced and no oxides of nitrogen. The yield of ozone rose steadily with increasing temperature, the maximum equilibrium amount being 1·5 per cent. by weight at an approximate temperature of 2200° C., a figure which bears a strikingly close agreement to that obtained by calculation from the electromotive force of the oxygen ozone cell. Taking $V_{0_3} = 0{\cdot}046$ volts, this corresponds to an equilibrium amount of 1·5 per cent. by weight at 2048° C.

Utilising an arc in liquid air a mixture of ozone and nitrogen peroxide was obtained which frequently exploded when attempts were made to separate the residual oxygen.

(B.P. O_3 = 120° C., O_2 = 182·7°)

The maximum yield of ozone obtained by means of a glowing Nernst filament in liquid oxygen was 10 mgms. in twenty-five minutes with a current consumption of 0·25 amperes at 100 volts equal to a yield of 3·5 grams of ozone per kilowatt hour.

Fischer having thus demonstrated the thermal production of ozone with the aid of liquid air, proceeded to extend Clements' experiments on the production of ozone by passing air at a high flow rate over a glowing Nernst filament. We have already noted that Clements was not able to detect the thermal synthesis of ozone with air-flows of linear speeds, up to 80 cms. per second. Fischer and Marx, using much higher velocities, showed that ozone was formed under these conditions and obtained a series of interesting results by studying the conditions of oxidation.

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When dry air is passed over a glowing Nernst filament two endothermic compounds may be formed, viz. nitric oxide and ozone. If moist air be employed the presence of hydrogen peroxide may likewise be demonstrated. The thermal equilibrium concentrations of nitric oxide, formed according to the reaction

$$N_2 + O_2 \rightleftarrows 2NO,$$

have been obtained by Nernst ("Göttingen, Nachricht.," p. 261, 1904) and Jellinek and Finck ("Zeit. Anorg. Chem.," 49, 212, 224, 1906) and are given in the following table :—

Temperature. °C.	*Per Cent. Concentration of NO in Air.*
1811	0·35
2033	0·67
2580	2·02
2675	2·35
3200	5·0

Jellinek (*loc. cit.*) likewise calculated the rate of decomposition of nitric oxide to its equilibrium value at various temperatures. Nitric oxide in this respect is markedly different from ozone since it is relatively much more stable at high temperatures; the times for the decomposition of half a given volume of NO to nitrogen and oxygen at atmospheric pressure are as follows :—

Temperature. °C.	*Time in Minutes to Effect 50 Per Cent. Decomposition.*
900	$7·35 \times 10^3$
1100	$5·80 \times 10^2$
1300	$4·43 \times 10$

Similar calculations can be made for hydrogen peroxide. We should therefore expect that with relatively low velocities of

air-flow over the glowing filament, only oxide of nitrogen should be obtained: with higher velocities mixtures of ozone and nitric oxide, and with very high velocities only ozone, since the rate of formation of nitric oxide is slower, but its rate of decomposition is much more than that of ozone. As will be observed from the following figures obtained by Fischer and Marx, this theoretical deduction is amply confirmed by experiment:

Flow Rate in Metres per Sec.	*Per cent. by Volume of Nitrogen Oxides*
2·8	[illegible]
6·2	[illegible]
10·5	[illegible]
16·2	[illegible]

At flow rates exceeding 30 metres per second no oxides of nitrogen could be detected in the air but ozone was always present. The yield of ozone was influenced both by the temperature of the glowing filament as well as by the linear velocity of the gas flow, as shown in the appended tables:—

Temperature of Nernst Glower in °C.	*Weight Per Cent. Ozone*	*Weight of Ozone Formed per Hour*	*Ozone in Milligrams Per Litre*
1171	0·0852	0·0126	0·4
1598	0·0986	0·0145	0·80
1667	0·0919	0·0252	0·80
1772	0·0936	0·0250	1·00
1822	0·0918	0·0245	1·15
1869	0·0238	0·1010	1·11
1930	0·0211	0·130	1·30

Velocity of Air in Metres Per Sec.	Weight Per Cent. O_3 in		Gms. O_3 Per Kw. Hr.
	Air.	Oxygen.	
	at 1800° C.		
30	0·011	0·019	0·29
44	0·019	0·082	0·85
57	0·021	0·091	1·15
64	0·019	0·080	1·28
75	0·012	0·052	1·07

In the presence of water vapour, the yields of ozone are considerably lower, and hydrogen peroxide is formed. The influence of the water vapour was likewise investigated by Fischer with the following results :-

Water Vapour Pressure in mm. Hg.	Wt. Per Cent. of O_3	Wt. Per Cent. H_2O_2 in 10 Litres.
0	0·0219	—
0·007	0·0176	—
5·0	0·00205	—
10·0	0·00136	0·011
14·1	0·00105	0·031
119·2	0·00076	0·074

According to this investigator, the function of the water vapour when present in but small quantities is purely catalytic in depressing the yield of ozone by accelerating the normal decomposition according to the equation—

$$2O_3 \rightarrow 3O_2.$$

When present in large quantities a reversible equilibrium obtains as follows :—

$$O_3 + H_2O_2 \rightleftarrows H_2O + O_2 + 2O.$$

Nernst (*loc. cit.*) has calculated that the ratio of the equili-

brium concentrations of O_2 and O formed according to the reversible equations

$$O_3 \rightleftarrows O_2 + O,$$
$$O_2 \rightleftarrows O + O,$$

is as 10^{23} to 1 or atomic oxygen is present in almost vanishingly small concentrations; consequently, in the above reaction the yield of ozone and of hydrogen peroxide is extremely small. Fischer was thus able to prepare ozone, nitric oxide, or hydrogen peroxide, all endothermic compounds, from air and water vapour at will by controlling the conditions so as to take advantage of the different rates of formation and decomposition of these substances at definite temperatures.

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CHAPTER V.

THE ELECTROLYTIC PREPARATION OF OZONE.

As early as 1801 Cruickshank drew attention to the fact that electrolytic oxygen, generated by the electrolysis of dilute sulphuric acid at insoluble anodes, frequently contained ozone.

Schönbein ("Ann. Phys. Chem.," **50**, 616, 1840) showed that the optimum yield of ozone was obtained when the sulphuric acid electrolyte contained 23·5 to 26·9 per cent. of sulphuric acid; solutions of phosphoric acid when submitted to electrolysis likewise yielded small quantities of ozone in the anodic oxygen.

De Marignac ("C.R.," **20**, 808, 1845) appears to be the first to point out the necessity of using cool electrolytes for the production of ozone; similar observations were made by Williamson ("Mem. Chem. Soc.," **2**, 395, 1845), H. Meidinger ("Ann.," **88**, 57, 1853), and Baumert ("Phil. Mag.," **4**, 6, 51, 1853).

The next advance to be recorded was the observation of H. Meidinger ("J.C.S.," **7**, 151, 1854) that small anodes were essential for the economic production of ozone. With the aid of an electrode only 20 mm. long by 0·5 mm. wide, in a sulphuric acid electrolyte of density 1·9, he obtained 0·3 per cent. ozone in the anodic oxygen.

Soret ("Pogg. Ann.," **92**, 504, 1854), showed that the

quantity of ozone liberated in the oxygen was determined by various factors. As electrode material, bright platinum, gold or platinum iridium were found most suitable, since other electrode materials, such as silver, black platinum, or oxide anodes, such as lead, iron or manganese, exert a very considerable activity in the catalytic decomposition of any ozone which might be formed at the surface.

The temperature of the sulphuric acid electrolyte and also of the anode itself plays an important part in obtaining relatively large yields of ozone. Soret (*loc. cit.*) obtained the following ozone concentrations, when using constant currents and electrolyte composition:—

Temperature.	*Grams Ozone per Cubic Metre.*
21° C.	14
17° C.	27
6° C.	60

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De la Coux ("L'Ozone," p. 79) gives the following values for the volume percentage of ozone liberated in the oxygen at different temperatures:

Electrolyte $H_2SO_4 : H_2O :: 1 : 5$

Temperature.	*Volume Per Cent. of Ozone.*
Room	0·4
5° C.	1
Ice and salt freezing mixture	2

Andrews ("Phil. Trans.," 1, 1850), utilising 20·81 per cent. sulphuric acid as electrolyte and a bunch of platinum wires as anode, kept cool during electrolysis by immersion of the cell in ice water, obtained 0·85 per cent. ozone. Schöne ("Ber.," 6, 1274, 1873) claimed the production of 3·29 to

8·6 per cent. ozone, and Carius ("Ber.," 174, 1, 1874), 3·44 per cent. of ozone by similar means.

Berthelot in 1878 ("C.R.," 86, 74, 1878) observed the formation both of ozone and hydrogen peroxide in sulphuric and other electrolytes and that high anodic current densities were essential for the production of ozone. The conception of anodic current density as distinct from the utilisation of small anodes marked a fundamental advance in the electrolytic synthesis of ozone.

Persulphuric acid ($H_2S_2O_8$) is simultaneously produced when very concentrated electrolytes are employed.

The investigations of Berthelot were continued by Richarz ("Wiedemann Annalen.," 24, 183, 1885; 31, 912, 1887), who determined the yields of ozone, persulphuric acid and hydrogen peroxide respectively with various current densities and varying sulphuric acid concentrations at 0° C. It will be noted from the following tables that Richarz confirmed the previous observer's results as to the necessity of high anode current densities and relatively concentrated electrolytes :—

Calculated Volume of O_2 Liberated during a Definite Time. Litres.	*Yield of Oxygen in the Form of :*	
	Ozone. Litres.	*Persulphuric Acid. Litres.*
2·1	—	0·03
3·71	—	0·40
7·47	—	2·32
17·12	0·04	8·08
30·0	0·11	16·25
45·4	0·26	24·70
65·7	0·61	39·00
95·0	1·1	45·60

Per Cent. Sulphuric Acid.	Yield of Ozone.	Yield of Persulphuric Acid.	Yield of Hydrogen Peroxide.
		In Terms of Oxygen.	
	Litres.	*Litres.*	*Litres.*
10·1	0·11	0·62	0
19·8	0·18	6·54	0
30·1	0·11	16·75	0
39·8	0·11	23·03	0
50·7	0·13	18·70	0
60·0	0·08	1·05	0·51
69·1	0·09	1·14	0·11
77·6	0·06	2·56	1·17
89·1	0·07	1·31	1·61

McLeod ("Trans. Chem. Soc.," 44, 51, 1883) conducted a very thorough investigation into the electrolytic preparation of ozone, he showed the importance of the various factors, viz. acid density, temperature of the solution and current density to which attention had been drawn by previous investigators.

From the following figures the extraordinary good yields obtained by McLeod are evident:

Electrode Material.	Density of Acid	Per Cent. Ozone by Volume.	Current Density Amps. per Sq. Cm.
6 platinum wires . . .	1·07	1·36	50·7
1 mm. long by 0·015 mm. diameter . . .	1·07	16·7	50·6
	1·35	0·5	50
6 platinum wires . . .	1·2	16·7	50
6 mm. long by 0·015 mm. diameter . . .	1·0	0·6	50

The influence of the acid density on the production of available oxygen in the electrolyte in the form of persulphuric acid and hydrogen peroxide was likewise investigated, the optimum production occurring with an acid density of specific gravity 1·20 with a current density of 50 amps. per

sq. cm., as is evident from the following figures taken from McLeod's data: —

Current Density Amps./Sq.Cm.	*Acid Density.*	*Mols. active O_2 Per 100 Mols. H_2 evolved.*
54	1·05	11·08.
53	1·10	20·80
54	1·15	25·8
53	1·20	34
50	1·25	29·9

With the introduction of the ionic theory by Arrhenius and van't Hoff in 1887 a more systematic investigation of the anodic reactions taking place during the electrolysis of dilute sulphuric acid was commenced.

It was shown that if the potential difference between two platinum electrodes in dilute sulphuric acid be gradually raised and the current intensity be plotted against the applied electromotive force a series of breaks occurs, which breaks, on the ionic theory, correspond to different anodic ionic discharges, the discharge of hydrogen being the only cathodic reaction. Careful investigation has shown that the ionic discharges associated with each break in sulphuric acid and electrolyte are as follows :—

P. D.	*Anodic Discharge.*
1·08	$O'' \rightarrow O_2$
1·07	$2OH' \rightarrow O_2 + H_2O$
1·95	$SO_4'' \rightarrow H_2SO_4 + O_2$
2·60	$HSO_4' \rightarrow (HSO_4)_2$
2·83	$3O'' \rightarrow O_3$

In 1889 Nernst, by the introduction of the conception of electrode solution pressure, pointed out the method of determining the influence of the anode potential on the discharge

of anions without having to take into account any cathodic reactions.

If a platinum electrode be saturated with oxygen under a definite pressure at a temperature of T°, and immersed in a sulphuric acid electrolyte, normal in respect to its hydrion concentration, electrical equilibrium will finally be arrived at between the oxygen molecules, atoms and ions in the electrode and electrolyte, the electrode becoming positively charged relatively to the solution by the discharge of negatively charged oxygen ions.

$$\begin{array}{c} +\ \text{ve} \\ + \\ + \\ + \\ + \\ + \end{array} \qquad \rightarrow O''$$

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and a condition of equilibrium will obtain when the potential difference between solution and electrode becomes sufficiently great to prevent the discharge of any more negative ions.

If V be the electrode-electrolyte potential difference, μO_2 and $\mu O''$ the molecular chemical potentials of the oxygen gas in the electrode and of oxygen ions in the solution, then if we imagine the transfer of a quantity of electricity $\delta\epsilon$ from electrode to solution, the electrical work will be equal to $-V\delta\epsilon$, the change in molecular chemical potential per mol. will be $\mu O_2 - 2\mu O''$, therefore, the work done on the transfer of this quantity of electricity is equal to

$$\frac{1/2\mu O_2 - \mu O''}{2\epsilon}\,\delta\epsilon$$

where ϵ is the charge associated with one gram ion of a monovalent element.

If the conditions of reversible equilibrium obtain, then

$$V\delta\epsilon = \mu O'' - \frac{1/2\mu O_2}{2\epsilon}\delta c.$$

Now $\mu O_2 = T(\phi O_2 + R \log \pi O_2)$ for a dilute solution, where ϕ is independent of the concentrations, it being merely a function of the temperature,

similarly $\mu O'' = T(\phi O'' + R \log (O''))$.

$$\therefore V = T\left\{(\phi_c'' - \frac{1/2\phi O_2)}{2\epsilon}\right\} + R \log \frac{O_c''}{\sqrt{\pi O_2}}\Bigg\}$$

$$= V_c + \frac{RT}{2\epsilon} \log \frac{O''}{\sqrt{\pi O_2}}.$$

Further, since in aqueous solutions

$$\mu O'' + 2\mu H = \mu H_2O,$$

$$V = V_c + \frac{RT}{2\epsilon} \log \frac{1}{C^2H\sqrt{\pi O_2}},$$

which gives an expression for the variation of the oxygen electrode potential, with alteration in the hydrion concentration of the solution and the pressure of the oxygen gas.

The value of V_c is approximately − 1·35 volts, whence the value of the cathode potential for a hydrogen electrode in normal hydrion solution under a pressure of one atmosphere is + 1·08 − 1·35 = − 0·27 volts.

If an oxygen electrode be set up against an ozone electrode, the difference in potential between the two electrodes can be calculated in a similar manner and found equal to:—

$$V_c' + \frac{RT}{2\epsilon} \log \frac{\pi O_2}{\pi O_3}.$$

Luther and Inglis ("Zeit. f. Physik. Chem.," 43, 203, 1903) first attempted to obtain an approximate value for V_c' by

measurement of the potential difference between an oxygen and an ozone charged platinum electrode immersed in dilute sulphuric or nitric acid. They obtained the value :—

$$V_{O_3} = -0{\cdot}736 \text{ volts.}$$

We have noted that approximately the same value, viz. −0·83 volts, can be obtained by calculation from the Nernst heat theorem. Subsequent investigators have found considerably lower values: Nernst ("Zeit. Elektrochem.," 9, 89, 1903) obtained the value $V = -0{\cdot}57$, and Fischer and Braune ("Ber.," 34, 3631, 1906) the values −0·61 to −0·46 volts. It would appear from the experiments of these latter observers on the thermal equilibrium, that the lower value, viz. −0·50 volts is probably more correct. It is possible that the higher values obtained by the earlier experimenters were occasioned by the presence of oxozone (O_4) in the ozone round the electrode, and a reinvestigation of this electrodic reaction is clearly eminently desirable.

From the above calculation it is evident that an extremely high anode potential is required to remove the formation of ozone, whilst, in order to ensure its stability when produced, both electrode and electrolyte must be kept cold. Fischer, Massenez, and Bendixsohn ("Zeit. Anorg. Chem.," **52**, 202, 1907; **II**, 229, 1907; **61**, 13, 153, 1909), realising these important factors, improved upon McLeod's results by adopting the artifice of water-cooled electrodes, in addition to the supplementary cooling of the electrolyte.

In their earlier experiments, a small platinum tube 6 mm. long was sealed to two terminal glass tubes and served as anode; the tube itself was covered with glass with only a thin strip, 0·4 mm. wide, exposed to the electrolyte.

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Cold water was circulated through this anode, and the electrolyte was kept cool by immersion in ice water.

Utilising an anodic current density of 58 amperes per sq. cm., and a sulphuric acid concentration of density 1·075 to 1·10, a yield of 17 per cent. ozone by weight (11·3 per cent. by volume) was obtained in the anodic oxygen.

A glass-covered, rhomboidal, platinum tube was then substituted for the cylindrical one, and one edge, 0·1 mm. in width, was exposed by grinding away the glass. The length of the tube was 11·5 mm., and it was maintained at − 14° C. by circulation of a solution of cold calcium chloride. A yield of 28 per cent. ozone by weight (19 per cent. by volume) was thus obtained. By embedding platinum foil in glass, and exposing one edge only, 0·01 mm. wide, to the electrolyte, slightly lower yields were obtained, viz. 23 per cent. of ozone by weight.

In confirmation of McLeod's results, the optimum concentration of sulphuric acid lay between = 1·075 and 1·10.

They noted that the quantity of ozone produced per kw. hr. rose steadily with continued use of the platinum, which became quite bright and burnished by the gas evolution in course of time.

A yield of 7·1 gms. per kw. hr. was obtained at a potential difference of 7·5 volts, and an anodic current density of 80 amperes per sq. cm. If we calculated the theoretical production of ozone per kw. hr. from its heat of formation, i.e. 34,000 calories, the yield of 7·1 gms. per kw. hr. indicates an electrical efficiency of only $\frac{7·1}{1200} = 0·6$ per cent.

F. Fischer assumed that the primary discharge of ozone occurs according to the equation

$$3O^{-} \rightarrow O_3 + 6\ominus,$$

which ozone is partly decomposed by the catalytic action of the anode surface.

Other, but less efficacious, methods have been suggested from time to time for raising the anode discharge potential, and thus increasing the yield of ozone. Newman and Gardner utilised a saturated solution of potassium permanganate in from 5 to 10 per cent. of sulphuric acid, and obtained relatively high concentrations of ozone; chromic acid can likewise be substituted for the permanganate.

St. Edme adopted the somewhat ingenious method of obtaining a high anode current density, by employing moistened crystals of phosphoric acid, or caustic potash or soda, as the electrolyte.

In this way, the electrolyte was given sufficient conductivity for passage of the current, yet at the same time only point contact between the moistened crystals and the anode was ensured.

Archibald and von Wartenberg ("Zeit. Elektrochem.," 17, 812, 1911) pointed out that the low yields of ozone accompanying the electrolytic decomposition of dilute sulphuric acid were probably occasioned by the high degree of anodic polarisation that was produced when operating at high current densities. In agreement with Fischer they considered that the primary formation of ozone takes place according to the equation—

$$3O^{-} \rightarrow O_3 + 6\ominus,$$

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ut that the subsequent catalytic decomposition of ozone at he electrode surface

$$2O_3 \rightarrow 3O_2$$

as not the most important factor. It was suggested that ie ozone thus formed is further oxidised at the anode—

$$O_3 + O'' \rightarrow 2O_2 + 2\ominus,$$

onsequently, if the anodic polarisation could be diminished ithout alteration of the anodic current density, increased ields of ozone could be obtained, since the secondary oxida- on would be diminished.

A series of experiments were carried out in which an lternating current was super-imposed on the direct current owing through the cell; this method of reducing the elec- ode polarisation having been utilised in the Wöhwill pro- ess for the electrolytic parting of gold and silver, and in the ectrolytic preparation of hydrogen peroxide. As electrodes, ort platinum wires or platinum capillaries cooled with ater were utilised, as electrolyte sulphuric acid of varying nsity, whilst a direct and alternating current of variable riodicity was applied simultaneously to the cell.

It was established that the optimum acid density varies ith the area of the electrode and not only with the current nsity, more concentrated electrolytes being desirable for g electrodes as indicated by the following figures:—

Area of Electrode in Sq. Cm.	*Optimum Acid Density.*
0·041	1·34
0·333	1·478

ie yield of ozone was also affected by the periodicity of the

alternating current, especially with current of low frequency; above 20 periods per second the effect was not so marked.

Direct Current.	*Alternating Current.*	*Periods per Second*	*Per Cent. O*
Amperes.			
0·61	0·20	11	1·04
0·61	0·50	17	4·10
0·61	0·60	25	4·77

It was noted that the applied potential difference necessary for the passage of the current rose until the ratio

$$\frac{\textit{alternating current}}{\textit{direct current}}$$

exceeded 3, and then rapidly sunk until this ratio became equal to 6, which was found to be an optimum. The potential difference was found to sink with increasing current density.

Their optimum yield was obtained under the following conditions:—

Electrode area: ·0333 sq cm periodicity 18 v per sec.

Temperature: 10° C

Acid density: 1·478

Direct Current.	*Alternating Current*	*A.C. D.C.*	*Anode Current Density*	*Per Cent. O, by Volume Calculated on the Direct Current.*
Amperes.				
0·25	1·50	6	0·75	17

The most important result from a technical point of view was the effect of the alternating current on the potential

difference necessary to effect the passage of this current; in the above case only 2·75 volts being necessary with an anode potential of 0·71 volt as opposed to 7·5 volts required by F. Fischer for direct current. We can calculate from the above data the production of ozone per kw. hr. as follows: 96,540 coulombs or 26·8 ampere hrs. liberate 1 gm. equivalent, or 11·2 litres of oxygen gas. Under the conditions of operation, however, the liberated gas contains 37 per cent. of ozone which would result from the condensation of 55·5 per cent. (37 per cent. + $\frac{1}{2}$ 37 per cent.) of the oxygen, which weighs 4·40 gms. Hence 26·8 ampere hrs. liberated 4·40 gms. of ozone. The potential difference which has to be applied to the cell to effect this liberation is 2·75 volts, thus 4·4 gms. of ozone are produced by the expenditure of energy equal to 26·8 × 2·75 or 73·7 watt-hrs., representing an output of 59 gms. per kw. hr., or over eight times the yield. This yield approximates to those obtained by the method of the silent discharge, and it would appear possible, if larger electrodes, and a cooled electrolyte were employed, to develop this method of producing ozonised oxygen both for strong and weak gas concentrations for the purposes of technical production.

CHAPTER VI.

PRODUCTION BY ULTRA-VIOLET RADIATION.

In 1900, Ph. Lenard ("Ann. der Physik," **1**, 480, 1900), utilising a quartz mercury vapour lamp as a source of energy, showed that ultra-violet light of extremely short wave length was an effective agent for ozonising oxygen. Both Lenard and E. Goldstein ("Ber.," **36**, 3042, 1913) showed that ultra-violet light in the Schumann portion of the spectrum within the spectral region $\lambda = 120\ \mu\mu$ to $\lambda = 180\ \mu\mu$ exerted the maximum activity in this respect; Goldstein (*loc. cit.*) actually obtaining pure liquid ozone by means of a quartz vacuum tube. Regener ("Ann. der Physik," **20**, 1033, 1906), who reinvestigated the matter, noticed the interesting fact that although light of wave length $\lambda = 120\ \mu\mu$ to $180\ \mu\mu$ was a powerful ozonising agent, yet light still in the ultra-violet portion of the spectrum of wave length λ 230 $\mu\mu$ to $\lambda = 290\ \mu\mu$ (especially $\lambda = 257\ \mu\mu$) exerted an equally effective catalytic decomposing effect. Ozone is thus formed by light of short wave length and decomposed again by light of slightly longer wave length. According to E. Warburg the ozonisation effected by ultra-violet light likewise increases steadily with the pressure of the gas ("Deut. Phys. Ges. Vehr., **17**, 10, 184, 1915).

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EFFECT OF RADIATION OF SHORT WAVE LENGTH.

Since marked concentrations of ozone result when oxygen is subjected to irradiation in light of this wave length, it necessarily follows that the energy necessary for the formation of ozone from oxygen is derived from the light, the process of ozone formation being a typical photo-chemical synthesis.

According to Planck's quantum theory ("Vorlesungen über die Warmestrahlung," M. Planck, Leipzig, 1906, pp. 100, *et seq.*), radiant energy is discrete, and can only be emitted by an oscillator or absorbed by a resonator in definite quanta.[1] The magnitude of the quantum bears a definite relationship to the frequency, of the light $\epsilon = h\nu$, where ϵ is the magnitude of the quantum, ν the light frequency, and h Planck's constant equal to $6{\cdot}85 \times 10^{-27}$ erg seconds.

Quanta, or the units of energy, may be emitted or absorbed in single units or in even multiples of that unit at a time. Two hypotheses have been advanced to explain the directional motion of the quanta since it is evidently rectilinear in motion. A. Einstein ("Ann. der Physik," **17**, 133, 1905) postulates an entity for the quantum in the form of a light cell which moves uniformly in the direction in which its centres of gravity is projected. Sir J. J. Thomson ("Proc. Phys. Soc.," **14**, 540, 1908; "Phil. Mag.," **792**, 1913) has advanced the ingenious hypothesis which assumes that the light travels in the wave form as postulated on the old hypothesis, but that these waves are confined to certain directions, being virtually

[1] It is, of course, possible, and indeed more probable, to assume that radiant energy appears discrete because matter is discrete, and that the radiation itself is continuous.

kinks in Faraday tubes which project from the point source. A beam of light is thus compared to a bundle of a number of Faraday tubes, and light transmission is effected by transmission of pulses naturally of definite magnitudes, and therefore in quanta along these tubes.

The elements when raised to a high temperature emit light in the form of spectral series. In all elements two distinct types of light emission can usually be observed, namely, band spectra and line spectra. Various investigators, notably H. Delandres ("C.R.," **100**, 1256, 1885, *et seq.*) have shown that the elementary band spectra can be divided into groups related by the expression $\nu = Bn^2 + \beta$, where β and B are constants, and n a series of integers, whilst in each group the frequency of the bands ν_0 are also related by the expression :—

$$\nu_0 = A\,(m + a)^2 + d,$$

where A, a, d are constants, and m a series of integers. Again, in the line spectra, J. J. Balmer ("Verh. d. Natur. ges. Basel," **2**, 648, 750, 1885; "Wied. Ann.," **25**, 40, 1885), C. Runge ("B.A. Reports," **576**, 1888), F. Paschen ("Ann. der Physik," **27**, 537, 1908, **35**, 860, 1911), and J. R. Rydberg ("K. Svenska, Vet. Akad. Handl.," **23**, 155, 1890) have shown similar relationships.

From these and other considerations (see J. J. Thomson, "Proc. Roy. Soc.," **14**, 540, 1908; "Phil. Mag.," **19**, 331, 1910); J. Stark ("Prinzipien der Atomdynamik," Leipzig, 1911) we deduce that a chemical element is not composed of homogeneous atoms or molecules, but that each atom or molecule is composed of at least two parts, one which gives rise to a line spectrum, and the other to a band spectrum

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when excited. The light thus emitted is periodic in character, being produced by some form of oscillation or oscillators, each periodic movement corresponding to one series of bands, or lines in the spectrum.

From other considerations, such as the electrical properties and radioactivity of certain elements, the composite nature of the atom receives confirmation.

Sir J. J. Thomson, who first suggested this actual structure for the atoms, although speculations on the electrical nature of matter had long been made for the purpose of calculation, assumed the existence of a relatively large positive nucleus with the negative electrons (or corpuscules) distributed in it. A small positive nucleus with the electrons rotating round it, in fact a small planetary system, is now a common hypothesis. It is at present uncertain whether the inverse square law or some higher power such as the inverse fifth power conditions the rotation of the electrons. Information is also lacking whether the electrons rotate in big or small circles, i.e. whether the plane of their rotation passes through the centre of gravity of the atom or not, and it is also a matter of speculation whether the electrons are point charges, or consist of rings such as are found in the satellites of Saturn.

It can easily be shown (see F. A. Lindemann, "Verh. d. Phys. Ges.," **13**, 482, 1911) that the amplitude of the vibrating particle in the oscillator emitting light radiation is of the order 10^{-9} to 10^{-10} cms., or from 10 to 100 times smaller than the actual diameter of an atom; we are therefore forced to the conclusion that the oscillators, both for the band and line spectra emissions, are to be found in the atom itself. Much evidence has been adduced to show that the source of

infra-red radiation is the atom, of the visible light the charged atom, and of the ultra-violet light the electron, the band spectra owing their origin to the oscillations caused by the swing of a valency electron about the positive nucleus.

If we imagine a valency electron circulating in its orbit with a definite and constant momentum, a definite amount of energy E must be supplied to remove the electron from the system. If the electron be nearly but not quite removed from the sphere of action of the atom it will oscillate about its mean position of rotation and emit light. The energy of oscillation must, according to Planck's hypothesis be a multiple of quanta, or :—

$nh\nu$ where n is a whole number, h Planck's constant, and ν the light frequency.

hence E must be $\geqq nh\nu$ to cause deformation and light emission; the smallest value of n is unity, so to cause light emission by deformation of the orbit of a valency electron—

$$E = h\nu,$$

or ν must be less than $\frac{E}{n}$. It necessarily follows that as E, the energy of deformation, is decreased, the wave length of the light will increase or be shifted towards the infra-red portion of the spectrum. The band spectrum of an element thus, according to this view, optically expresses the configuration of the valency electrons in the molecular system.

The relationship between position of the band spectrum and complexity of the molecule in which the valency electron is oscillating, can be clearly shown in the case of oxygen.

Monatomic oxygen, viz. O, has a band spectrum in the region $\lambda = 245\ \mu\mu$ to $\lambda = 333\ \mu\mu$ (W. Steubing, " Ann. der

Physik," **33**, 353, 1913). In diatomic or molecular oxygen, viz. O_2, the band spectrum is shifted towards the ultra-violet, viz. $\lambda = 120\ \mu\mu$ to $\lambda = 190\ \mu\mu$, since the energy E, required to remove a valency electron from two positive nuclei, is much greater than is required to remove one of the two valency electrons from the single positive nucleus of the atomic oxygen. In ozone, on the other hand, not only is it evident from its endothermic character, but also from a visual representation of three positive nuclei coupled by valency electrons, that the energy required to remove a valency electron from the ozone molecule will be less than from the molecular form, i.e. the band spectrum will be between the two former. In fact, a strong absorption is noted at $\lambda = 258\ \mu\mu$ (W. N. Hartley, "Chem. News," **42**, 268, 1888).

The oscillator of the series spectrum, on the other hand (J. Stark, "Die Elektrizität in Gasen," Leipzig, p. 447, 1902), is to be found in the positive ion resulting from the complete removal of a valency electron from an atom or a molecule. The notable experiments of Sir J. J. Thomson ("Phil. Mag.," **13**, 561, 1907, **21**, 275, 1911, *et seq.*) on cathode ray analysis have indicated that such ions which have lost or gained a valency electron possesses actual entities, and can be distinguished one from another by their difference in electrical charge; thus in the case of oxygen there have been isolated the charged gas ions :—

$$\overset{++}{O},\ \overset{+}{O},\ \overset{-}{O},\ \overset{--}{O},$$

as well as oxygen molecules of various charges.

F. Horton ("Phil. Mag.," **22**, 214, 1914) has identified as carriers of positive electricity, giving positive band spectra in

oxygen, the following polymers of electric atomic weights 8, 16, 32, 48, 96.

N. Bohr ("Phil. Mag.," **26**, 476, 1913) attributes to the oxygen atom a nucleus carrying eight unit position charges with eight electrons, of which only two appear removable by methods at present available.

The Mechanism of Ozone Formation.

We have already noted that the oxygen molecule when subjected to ultra-violet light radiation of the correct frequency for resonance may absorb quanta of energy. Similar conditions obtain for the iodine molecule in the infra-red spectral range and we may regard the primary cleavage to occur in a similar manner, viz. :—

$$I_2 \rightleftarrows I + I$$

$$O_2 \rightleftarrows O + O.$$

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Warburg ("Preuss. Akad. Wiss.," Berlin, 872, 1914) has adopted this hypothesis to explain the mechanism of ozone formation. He assumes that the atomic oxygen resulting from the cleavage of the molecule secondarily reacts either with atomic oxygen to reform molecular oxygen as indicated by the reversibility of the above equation, a point clearly emphasised by Nernst from thermal considerations (see p. 29), or it may react with molecular oxygen to form ozone—

$$O_2 + O = O_3.$$

Warburg's experiments, conducted under pressures of from 30 to 400 kgm. per sq. cm., yielded a photo-chemical efficiency of 55 per cent. at 120 kgm. cm.^{2} and 29 per cent. at 300 kgm. cm.^{2}, indicating the plausibility of the above hypothesis. Weigert ("Zeit. Wiss. Photochem.," **11**, 381, 1912) obtained

a photo-chemical efficiency of 46·0 per cent. and a thermo-dynamic efficiency of 27·7 per cent.

The reaction is primarily a molecular one and the energy of formation of a gram. mol. of O_3 (34,000 cal.) should have its corresponding photo-chemical equivalent equal, as calculated by Warburg, to $Nh\nu$ where N is the number of molecules per gram. mol. From the relationship

$$\underset{\text{(cal.)}}{Nh\nu} = \frac{2{\cdot}73}{\lambda \text{ in cm.}}$$

with a value of 34,000 calories for the heat of formation of ozone we obtain $\lambda = 800\ \mu\mu$, as the critical ozonising wave length, or we must assume that one quantum of $\lambda = 200$ will form four ozone molecules.

Ozone formation may therefore occur without gas ionisation, a fact which was first demonstrated by Lenard and confirmed by Ludlam ("Phil. Mag.," 23, 757, 1912).

We can easily deduce from our previous considerations on the mechanism of photo-chemical processes in the light of the quantum theory that ionisation of oxygen will be brought about by light of shorter wave length than that required to produce atomic oxygen and hence ozone.

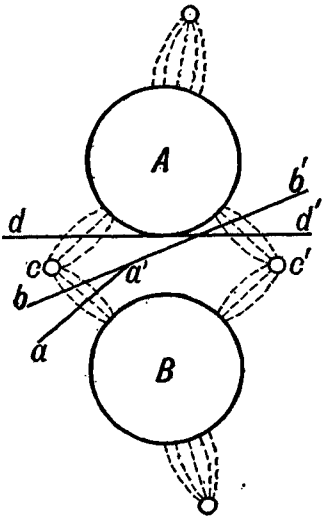

FIG. 4.

If A, B, represent the two positive nuclei of oxygen atoms in a neutral molecule and c, c', one valency electron of each atom which has come within the attraction (partially saturated) of the positive charge of the

neighbouring atom; the simplest line of cleavage is along a, a', resulting in the formation of an oxygen molecule with one bond as link O—O, which can then react to form ozone—

$$3O—O \rightarrow 2O_3.$$

This requires the smallest amount of energy, and hence is effected by light of the longest wave length ($> \lambda = 200\ \mu\mu$). The simplest cleavage into neutral atoms takes place along the line b, b', requiring more energy than is necessary to effect partial unsaturation, and hence shorter wave length light $\lambda = 200\ \mu\mu$. Cleavage along the line d, d' necessitates the removal of one electron from an oxygen atom and consequent increase of energy or light of a still shorter wave length, ca. $\lambda = 180\ \mu\mu$. The energy required to move a valency electron which is partially attached to two atoms on to one atom is of the order 1×10^{-12} ergs, to completely remove the electron requires a considerably greater expenditure of energy. A quantum of light energy in the visible or ultra-violet portion of the spectrum is of the order of $> 3 \times 10^{-12}$ ergs; thus with very short wave length light electron removal can easily be effected.

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Under these conditions we obtain monatomic oxygen ions—

$$O_2 \rightleftarrows \overset{+}{O} + \overline{O}.$$

Ozone formation may result from this ionisation according to the following reaction :—

$$2O_2 + \overset{+}{O} + \overline{O} = 2O_3.$$

Light of still shorter wave length will actually remove electrons from the monatomic oxygen ion (Ca. $\lambda = 130\ \mu\mu$)

$$\overset{+}{O} \rightarrow \overset{++}{O} + \ominus,$$

which electron may attach itself to the charged − ve residue

provided that it be projected from the original ion with sufficient kinetic energy—

$$\bar{O} + \odot \rightarrow \bar{\bar{O}}.$$

Or again, it may attach itself more easily than as above to a neutral molecule—

$$O_2 + \ominus \rightarrow \bar{O}_2.$$

In this way we can imagine the formation of the various charged ions actually observed during irradiation of oxygen by ultra-violet light of short wave lengths within the range $\lambda = 130$ to 200 $\mu\mu$.

Construction of Apparatus.

(*a*) *Source of Ultra-violet Light.*—We have already indicated that for the production of ozone a source of ultra-violet light rich in lines of the Schumann region (below $\lambda = 200$) and if possible free from light of longer wave length, especially in the region $\lambda = 230$ to 290 $\mu\mu$, which exerts a strong catalytic activity in deozonisation.

A glance at the curves representing the distribution of energy over the spectrum radiated from a black body at various temperatures will suffice to indicate that "black body" radiation is unsuitable as an efficient source of Schumann light. In agreement with the theoretical calculations of Wien and Planck the experimental observations of Lummer and Pringsheim ("Ver. d. Deut. Phys. Gesell.," **1**, 23, 1899; **2**, 163, 1900) have indicated that, with elevation of the temperature of the radiator, the maximum energy emission E_m shifts from the longer to the shorter wave length portion of the spectrum. Even, however, at sun temperature, ca. 5500° C., which temperature can only be approached with difficulty by the utilisation of carbon arcs under high gas

pressures, a black body radiator will have its E position at about $\lambda = 500\ \mu\mu$, or in the green of the visible spectrum. The fraction of the total energy emitted which will lie in the Schumann region of the spectrum $\lambda 1$ to $200\ \mu\mu$ will be remarkably small.

We must, therefore, reject black body radiators and fall back on methods of obtaining selective emission and as such light sources we may utilise the arc, spark, or vacuum tube illumination of various elements.

Arc and Spark Light Sources.

Most metals exhibit strong Schumann and ultra-violet light radiation when the arc or spark electric discharge is made to pass between metallic electrodes.

We may argue from the electronic structure of the atom that since the removal of a second electron from an atom which has already lost one, necessitates the supply of a still greater quantity of energy for its removal than the first, and as this energy is supplied in quanta, the value of $h\nu$ must rise with each subsequent removal. Atoms which can loose many electrons without loss of atomic identity will therefore radiate light corresponding to high values of $h\nu$, i.e. of extremely short wave length.

The elements which have been most widely used as sources of ultra-violet light are those of aluminium, iron and especially mercury, which can loose as many as eight electrons.

The aluminium ultra-violet spectrum has been investigated, more particularly by Lenard ("Sitz. Heidelberg, Akad. Wiss. Abh.," 31, 1910) and Morris Airy ("Man. Lit. Phil. Soc.," XLIX, 1, 1905), and iron by Lyman ("Astrophys. Jour.," 38, 282, 1913).

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Much work has been accomplished on the mercury arc, which is especially rich, both in green, violet, and ultra-violet radiation, most conspicuous where mercury vapour lamps are used as light sources.

The investigations of Tian ("C.R.," **155**, 141, 1912) and Lyman ("Astrophys. Jour.," **38**, 282, 1913) have shown that "the spectrum is dominated by the broad unsymmetrical line $\lambda = 184{\cdot}96\ \mu\mu$". The spark spectrum of mercury is rich in lines, whilst the arc spectrum contains only a few. Other lines in the same series predicted by Paschen have likewise been observed at $\lambda = 140{\cdot}2\ \mu\mu$ and $\lambda = 126{\cdot}9\ \mu\mu$. When viewed through a short column of air the line $\lambda = 184{\cdot}96\ \mu\mu$ is replaced by three groups of faint lines observed by Steubing ("Ann. der Physik," **33**, 573, 1910). Ionisation of the mercury atom by collision commences at $\lambda = 253{\cdot}6\ \mu\mu$, equivalent to a fall of potential of the colliding electron of 4·8 volts—A. Lande ("Phys. Zeit.," **15**, 793, 1914), J. Franck and G. Hertz ("Deut. Phys. Ges.," **16**, 407, 1914).

Vacuum Tube Discharge.

Of the elements investigated by means of the vacuum tube discharge, the remarkable activity of mercury vapour in the emission of light of short wave length has already been discussed, two other substances also exhibit a marked selective emission in the ultra-violet region, namely hydrogen and carbon, the latter usually introduced into the vacuum tube in the form of one of its oxides, carbon monoxide or dioxide. Lyman ("The Spectroscopy of the Extreme Violet," Longmans, 1914) states that hydrogen surpasses all other gases in the wealth and strength of lines in the Schumann region. They extend at pressures of 1 to 5 mm. from

$\lambda = 90\ \mu\mu$ to $\lambda = 167{\cdot}5\ \mu\mu$, and this light forms one of the most important of all three distinct spectra which the element possesses. St. John ("Astrophys. Jour.," XXV, p. 45, 1907) found hydrogen to emit 250 times as much energy of short wave length as a mercury vapour lamp. There appears to be a distinct gap in light emission within the spectral region $\lambda = 167{\cdot}5\ \mu\mu$ to $\lambda = 243{\cdot}3\ \mu\mu$.

Delandres ("C.R.," **106**, 842, 1888) noted a great number of bands in the ultra-violet spectrum with the rarified oxides of carbon in the vacuum tube within the range $\lambda = 130\ \mu\mu$ and $\lambda = 210\ \mu\mu$.

When consideration is taken of the difficulties in the operation of an arc lamp with iron or aluminium electrodes, such as the automatic adjustment of the arc gap, the removal of the oxides produced during combustion, if the arc be open, or the volatilisation of the metals on to the walls, if the arc be of the enclosed type, as well as the great thermal effects produced by an arc lamp in continuous operation, which, as we have seen, militates against a high yield of ozone, it will be clear that the mercury vapour lamp operating at low voltages and relatively high internal mercury vapour pressures, or working at high voltages with only a few millimetres pressure of vapour, is the most suitable source of ultra-violet light which, up to the present time, has received systematic investigation.

The utilisation of hydrogen vacuum discharge tubes, however, may possibly receive more attention in the future, since discoloration of the tube walls, so frequently noticed in mercury lamps, would be greatly minimised (see also Lyman, "Astrophys. Jour.," **27**, 87, 1908).

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(*b*) *Material for Lamp Construction.*.

The walls of the mercury vapour lamp must be transparent to radiation of this extremely short wave length, in order that ozonisation of the surrounding oxygen may be effected. Ordinary glasses are singularly opaque, thus borosilicate crown-glass, which is the most transparent of the ordinary glasses, passes only 8 per cent. of light of wave length $\lambda = 309$ $\mu\mu$ (Krüss, "Zeit. f. Instrumentkunde," **23**, 197, 1903), and is opaque to light below $\lambda = 297$ $\mu\mu$. Schott of Jena's uviol glass was specially prepared by Zschimmer ("Zeit. f. Instrumentkunde," **23**, 360, 1903) for ultra-violet transparency. With a thickness of 1 mm. fifty per cent. transmission of light at $\lambda = 280$ $\mu\mu$ is effected, whilst a uviol microscope cover-slip is still transparent to $\lambda = 248$ $\mu\mu$. Zschimmer further indicated ("Phys. Zeit.," **8**, 611, 1907) that pure boric anhydride and silica are very transparent even below $\lambda = 200$ $\mu\mu$ (and even below $\lambda = 185$ $\mu\mu$), but that the addition of certain salts lessens their transparency. Boric anhydride is slightly inferior to silica, its lower limit of transparency, according to Lyman, being $\lambda = 170$ $\mu\mu$. Fritsch ("Phys. Zeit.," **8**, 518, 1907) gives the following composition of a glass extremely transparent down to $\lambda = 185$ $\mu\mu$:—

CaF_2	6 parts.
B_2O_3	14 ,,

M. Luckiesh ("J. Franklin Inst.," **186**, 111, 1918) claims that a special cobalt-blue glass is more transparent than ordinary glass to ultra-violet. With the exception of Fritsch's borate glass, which does not appear to have received any technical application as yet, extremely pure fused silica is the most suitable material for lamp construction.

Hughes ("Photo Electricity," 1913, p. 137) has shown that fused quartz is still transparent down to $\lambda = 145{\cdot}0$ $\mu\mu$; a thickness of 0·3 mm. will transmit 24 per cent. of $\lambda = 184{\cdot}9$ $\mu\mu$, 36 per cent. of $\lambda = 197$ $\mu\mu$, and 40 per cent. of $\lambda = 200{\cdot}2$ $\mu\mu$.

Mention may be made of the naturally occurring substances, which are even more transparent to ultra-violet light than fused silica, viz. quartz, fluorite, and rock salt. Quartz in very thin laminæ is transparent down to $\lambda = 145$ $\mu\mu$, rock salt to $\lambda = 175$ $\mu\mu$, and fluorite to $\lambda = 123$ $\mu\mu$.

In the Quain apparatus, which is the only form of quartz mercury vapour lamp ozoniser in technical use, the lamp which is of the vacuum type and operated by a coil or magneto, at a terminal potential difference of circa 7000 volts, is inserted in a hollow aluminium tube through which the air or oxygen, undergoing ozonisation by irradiation from the lamp, is passed at a relatively low velocity. No literature has been published dealing with the problem of the influence of gas velocity on ozone concentration and ozone production per minute, but the following considerations will indicate that the optimum conditions will very likely be formed when only a thin film of air passes over the lamp at high velocity. Dry and dust-free air is relatively transparent to light above $\lambda = 186$ $\mu\mu$, but nearly opaque to light below $\lambda = 178$ $\mu\mu$. Lyman ("Astrophys. Jour.," **27**, 87, 1908) states that 1 mm. of air will cut off most of the light below $\lambda = 185$ $\mu\mu$, which, as we have seen, is the active light for the production of ozone. Kreusler ("Ann. der Physik," **6**, 418, 1901) gives the following figures for the absorption produced by 20·45 cms. of oxygen :—

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Light of Wave Length.	*Per Cent. Absorption.*
186	32·5
193	6·2
200	negligible

whilst Schumann observed an air film only 4 mm. thick (equal to ·8 mm. of oxygen approximately) was sufficient to render all lines below $\lambda = 178$ $\mu\mu$ extremely faint. With 0·5 mm. of air, light down to $\lambda = 168$ $\mu\mu$ would be transmitted, and below 0·05 mm. in air thickness, the spectrum stretched considerably below $\lambda = 160$ $\mu\mu$. It will thus be observed that the ozonising action of ultra-violet light, in so far as it is caused mainly by light of wave length smaller than $\lambda = 200$ $\mu\mu$ is confined to but a millimetre thickness or so of air.

Lamp Efficiency.

Figures are not available as to the optimum conditions for the production of ultra-violet light from mercury vapour lamps. As is to be expected the ultra-violet light fraction increases with increasing voltage (see A. Tian., "C.R.," **155**, 141, 1912).

J. N. Pring ("Proc. Roy. Soc.," **96**, 204, 1914) showed that no oxides of nitrogen or hydrogen peroxide were formed during operation and that the average ozone content of the air in the neighbourhood of the lamp was 0·01 per cent. at 760 mm. and 0·0014 per cent. at 30 mm. air pressure. W. Chlopin ("Zeit. Anorg. Chem.," **71**, 2198, 1911), on the other hand, detected the presence of both hydrogen peroxide, ozone and nitrous anhydride by exposure for a few minutes of ordinary moist air to the rays of a Westinghouse quartz mercury vapour lamp.

The ultra-violet efficiency of the various types of mercury vapour lamps on the market was examined by C. Fabry and Buisson in 1911 ("C.R.," **153**, 93, 1911), who obtained the following results:—

Lamp.	*Percentage of Power Supplied, Radiated in Wave Lengths below 320.*
Westinghouse	6
A.E.G.	4·7
„	0·85
Westinghouse (Ii)	0·13

Production by Ionic Collision.

In the previous discussion we have noted that molecular cleavage of oxygen into neutral atoms with or without subsequent ionisation may be brought about by absorption of light energy, provided that this latter is of the correct frequency for absorption.

The production of ozone depends primarily on the simplest cleavage, viz:—

$$O_2 \rightarrow O + O,$$

with subsequent synthesis of ozone, whilst secondary ozone formation probably results from the combination of charged ions, e.g.:—

$$O_2 + \dot{O} = O_3$$

(see W. W. Strong, "J. Amer. Chem. Soc.," **50**, 101, 1913)

The cleavage and ionisation of the oxygen molecule may also be brought about by other means than by the absorption of light quanta, such as by direct impact by α particles or electrons.

Madame Curie noticed that radium salts were effective in ozonising oxygen ("C.R.," 183), a point at first disputed by

Ramsay and Soddy, but finally confirmed by Giesel and Nasini and Levi ("Atti. R. Accad. Lincei," **17**, 46, 1908). S. C. Lind ("J. Amer. Chem. Soc.," **47**, 397, 1912) and O. Schoner ("C.R.," **159**, 423, 1914) showed that the α particles projected from radium ozonised oxygen; Lind showed, *inter alia*, that the number of ozone molecules formed were equal to the number of ions made by the α particles—

$$O_2 \rightarrow O + O$$
$$2O_2 + 2O \quad 2O_3.$$

In many of his experiments a slight deficiency in ozone formation was observed from that calculated, but under no circumstances was more ozone than the theoretical obtained. (See also W. Duane, "C.R.," **153**, 336, 1911.) It may be noted in passing that similiar results were obtained for hydrogen by W. Duane and Wendt ("Phys. Rev.," **10**, 110, 1917), the presence of H_3 being clearly demonstrated. F. Krüger ("Phys. Zeit.," **13**, 1040, 1912) obtained ozone by the ionising action of Lenard rays obtained by the projection of cathode rays through an aluminium window and showed, as indicated in the following tables, that more ozone was formed per second than ions in oxygen, the number of molecules of ozone formed approximately more closely to the ionisation of nitrogen under similar conditions:—

No. Ions Produced per Sec. in $O_2 \times 10^{14}$.	*No. Ions Produced per Sec. in* $N_2 \times 10^{14}$.	*No. Mols.* O_3 *Produced per Sec.* $\times 10^{14}$.
0·70	6·0	7·0
0·56	1·2	1·1
0·41	1·4	1·4
0·21	0·5	0·33

In the case of radium, practically all the ozone produced is formed through the agency of the α particles, the β and γ

radiation producing but minor and secondary effects. The energy associated with each group of rays is clearly demonstrated from the following figures ("Phil. Mag.," **22**, 567, 1907) :—

Heating effect of 1 gm. radium = 110 gms. cal. per hr.

α rays	103·5
β ,,	2·0
γ ,,	4·5

With Röntgen or X-rays, on the other hand, ionisation is not so marked, since only about 1 atom in $12^{1\cdot 4}$ is ionised by the penetration of the rays into a substance.

For ionisation to be effected by collision, the molecule or atom must be struck by the α particle or electron with sufficient energy to discharge a valency from its normal orbit in the atomic sphere. It will thus leave the atom with a certain critical velocity which it would also acquire if it had been acted on by a definite potential difference. We may therefore equate the loss in kinetic energy sustained by the impinging α particle or electron as a result of collision with the molecule and the energy of discharge of the electron.

If m be the mass of the impinging electron, v_0 its incident and v_1 final velocity, its loss in kinetic energy will be: $1/2m(v_0^2 - v_1^2)$ whilst the discharged electron of charge e will possess an energy Ve.

$$\text{Hence } 1/2m(v_0^2 - v_1^2) = Ve.$$

A discharged electron or α particle will thus continue its passage through the gas, causing ionisation by collision on its way until its velocity sinks to the value v_2 where

$$1/2mv_2^2 = Ve,$$

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the minimum velocity necessary to cause ionisation by collision. Below this velocity the electron will merely adhere to a neutral molecule to form a negatively charged ion, the α particle will loose its charge to a neutral molecule to form an atom of helium and a negatively charged gas ion, provided that they have not come in contact with the walls of the containing vessel before their journey is completed.

In the case of ionisation by electrons the value of

$$\frac{e}{m} = 1{\cdot}77 \times 10^{7},$$

$$\therefore V \quad 2{\cdot}82 \times 10^{-16} v^2$$

$$\text{or } v \propto \sqrt{V}.$$

In the following table are given the electron velocities in cms. per second and the potential difference in volts required to bring them to rest:—

V.	v.
1	$5{\cdot}9 \times 10^{7}$
10	$1{\cdot}88 \times 10^{8}$
100	$0{\cdot}595 \times 10^{9}$
1000	$1{\cdot}88 \times 10^{9}$
10,000	$5{\cdot}95 \times 10^{9}$
100,000	$18{\cdot}8 \times 10^{9}$
200,000	27×10^{9}

For the minimum velocity required for an electron to cause ionisation of an oxygen molecule by collision Franck and Hertz ("Verh. d. Deut. Phys. Ges.," XV, 34, 1913) found the value $1{\cdot}80 \times 10^{8}$ cms. per second corresponding to a fall of 9·0 volts.

This value is in extremely good agreement with that calculated from the critical wave length requisite for ionisation by absorption of ultra-violet light quanta. It is evident that

the requisite energy equal to Ve can be supplied by the kinetic energy lost by an impinging electron, i.e. $1/2mv^2$, or by the absorption of a light quantum $h\nu$ thus—

$$Ve = 1/2m.v^2 = h\nu.$$

Taking $\lambda = 135\ \mu\mu$ we obtain the value 9·20 volts for the value of V determined in this manner. A value of 8·6 volts being obtained by Compton ("Phys. Rev.," 8, 412, 1916), by calculation of the work necessary to remove a valency electron from an atom possessing Bohr's hypothetical structure.

Quantitative agreement between the yield of ozone calculated and that actually obtained has, as has already been mentioned, been shown to hold for the case of ozonisation by α particle discharge by Lind. Cases of ionisation and ozonisation by electron emission have given more variable results. This is in part due to the great velocity and relatively small size of the electrons which can pass through a vessel containing gas and come to rest on the walls without having made a great number of collisions, thus the major part of its kinetic energy is still retained when it emerges from the gas and strikes the walls. Again, it appears that every collision which an electron makes with a molecule of oxygen, with sufficient energy to dissociate the molecule, is not always effective in doing so. According to P. Kirkby ("Proc. Roy. Soc.," 85, 151, 1911), only 50 per cent. of such collisions are effective. The yield of ozone by electron collision in oxygen, therefore, usually falls far short of the theoretical quantity.

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CHAPTER VII.

PRODUCTION BY MEANS OF THE SILENT ELECTRIC DISCHARGE.

THE formation of ozone by the action of the silent discharge on air is the only process of ozone production which has received considerable technical development and a great number of ozonisers of various types and designs have been incorporated in installations for the economic manufacture of ozone and ozonised air.

It may be stated at the outset that we do not possess sufficient information about the mechanism of the silent discharge to put forward a satisfactory explanation as to the *modus operandi* of a "Siemens tube," nor can it be said that the design and construction of ozonisers is on a scientific basis, since, with the exception of a few generalisations based on experiment and a few suggestions based upon somewhat unsatisfactory and frequently incomparable theories, ozonisers have been built on the rule of thumb and hit-or-miss principle.

The following considerations, however, will indicate in some measure the intricacy of the problem :—

If the potential difference between a point and a plate separated by a few millimetres of air space from it be gradually raised, the current potential difference curves be plotted, and they will be found to possess certain characteristic features for both direct and alternating currents. The V, *i* characteristic curves for point plate and plate discharges have been obtained with great accuracy by Toepler ("Drud.

Ann.," 7, 477, 1902) and Brion (" Zeit. Elektrochem.," 14, 245, 1906) for direct currents, and by Crump and Hoyle (" Electrochem. Ind.," 7, 74, 1909) for alternating currents.

The following indicate the series of changes in the character of the discharge obtained by Toepler :

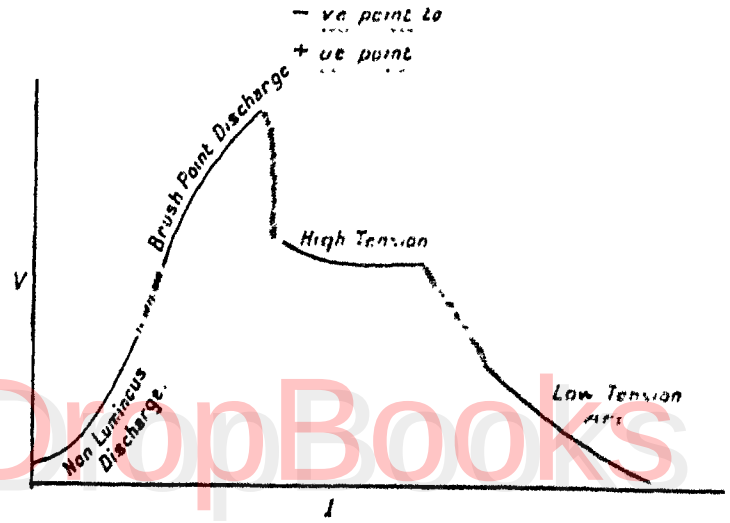

FIG. 5

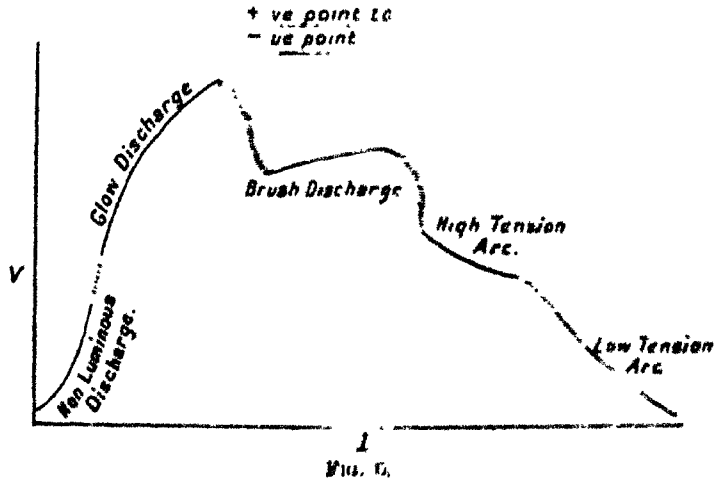

FIG. 6.

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If a very small potential difference be applied between a negative point and positive plate, a small amount will flow, the current being carried entirely by the negative ions present in the gas; the *i*, V curve will then follow Ohm's law until the rate of removal of gas ions by the electric current becomes equal to the rate of supply, when the so-called saturation current is arrived at, which is independent of the applied potential difference.

As the P.D. is gradually raised, negative electrons are discharged from the point and participate in carrying off the current. The area around the point now becomes luminous, which luminosity extends towards the plate with increasing P.D., the discharge becoming a typical brush accompanied by a slight crackling noise. At this point positive gas ions, produced at the anode by detachment of an electron from a gas molecule through collision with an electron travelling at high speed, will also augment the current capacity of the system.

The resistance of the air circuit now falls quite rapidly owing to increase in conductivity by collision between electrons and the gas molecules and the brush discharge is converted into a high tension arc discharge. During the high tension arc discharge, the cathode gets extremely hot owing to bombardment by positive ions and the thermionic emission of electrons as well as particles of vaporised electrode material charged positively commences, resulting in a still greater increase in conductivity; the high tension arc is therefore not stable but is transformed into the more usual low tension arc. For the production of ozone the electrically stable part of the discharge only, viz. the

non-luminous, the glow, and the brush discharge, come under consideration, since, as we have already had occasion to observe, the high thermal effects associated with both the high and low tension arc discharges are more than sufficient to mask any electronic formation of ozone.

We have noted that the transformation of the silent discharge into the high tension arc discharge occurs after the whole inter-electrode space has been filled with the discharge glow, which makes its first appearance in the so-called corona light. The nature of this luminescence is not clearly understood; that it is a function of the composition of the gas is shown by the experiments of E. Rosenfeld ("Z. f. Elektrochem.," 17, 725, 1911), who noted that the discharge is pink in nitrogen, blue in hydrogen, white in chlorine, "like the combustion of iron wire in oxygen," and greenish blue in oxygen.

Sir J. J. Thomson ("Conduction of Electricity through Gases," 1906, pp. 478-512) has shown that at the moment when both anode and cathode glow make their appearance there is a very great increase in conductivity of the gas space, and advanced the hypothesis that just prior to the appearance of the glow discharge the atoms have acquired internal energy by collision with electrons and by absorption of soft Röntgen rays, generated by collisions of electrons with other atoms, until it has nearly approached the critical value at which the atom becomes unstable and luminous, that ionisation precedes the luminous discharge was clearly indicated by D. Mackenzie ("Phys. Rev.," 5, 291, 1915).

According to K. Nesturch ("Phil. Mag.," 30, 244, 1915) there always exists a definite ratio between the amount of

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radiation and the number of gas ions formed by such collision.

Sir J. J. Thomson and R. Threlfall ("Proc. Roy. Soc.," 40, 340, 1886) clearly showed that ozone formation in the silent discharge tube was associated with the production of a luminous glow, whilst a similar conclusion was arrived at by E. Warburg ("Ann. der Physik," 17, 1, 1905), who advanced the hypothesis that ozone is only produced by electrons with sufficient kinetic energy to cause themselves to become luminous.

The view that the corona and brush discharges are at least in part due to ionisation by collision is supported by a series of experiments which have been made on the corona "pressure" phenomenon by S. P. Farnweld, J. Kunz, and especially Townsend and E. Warner ("Phys. Rev.," 8, 285, 1916). It is evident that if the molecules break up into ions as a result of ionic collision an increase of pressure should result. In an enclosed gas space subjected to the brush discharge, this pressure increase has actually been noted, and when corrected for the unavoidable temperature increase the following relationship was found to hold good :—

$$Vi = v_0 \delta p,$$

where V is the applied voltage, i the corona current, v_0 the volume of the gas subjected to the silent discharge.

In oxygen, however, there is scarcely any increase in pressure, due to the formation of ozone; in other words, the ozone formation is strictly proportional to the ionisation.

It would therefore appear that only a relatively small portion of the discharge is effective in the production of ozone and that the optimum results are to be obtained when

the ozoniser is so operated that the luminosity of the silent discharge glow is at a maximum.

Many conflicting statements have been published relative to the yield of ozone per kilowatt hour obtainable in ozonisers; on analysis these are found to be due to the fact that many investigators have ignored the primary consideration affecting the production of ozone by this means, viz. the relationship between ozone production per kilowatt hour and the concentration of the ozone. It is evident that if a definite volume of air be subjected to the silent electric discharge, the ozone concentration in that air will rise to a certain definite value, C_n, the "limiting" concentration. When this concentration is reached, the rate of formation of ozone $\frac{dc_3}{dt}$ will be equal to its rate of destruction by thermal, catalytic and other effects. Thus, in the enclosed volume of air, the apparent ozone production per kilowatt hour will be zero whilst the actual production will be $\frac{dc_3}{dt}$. As a first approximation it may be taken that the rate of catalytic decomposition is proportional to the concentration of ozone or $\frac{dc_3}{dt} = KC_3$, thus the energy required to produce strong concentrations of ozone in a stream of gas will be a great deal more than is necessary to produce the same amount of ozone in a very dilute state.

As clearly pointed out by Allmand ("The Principles of Applied Electro-Chemistry"), the duty of an ozoniser cannot be obtained without a knowledge of the following data:

(1) The limiting yield, or the yield per ampere hour at zero concentration.

(2) The maximum concentration of ozone obtainable.

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(3) The rate of variation of the yield with the concentration.

Influence of Current on Yield of Ozone.

Owing to the difficulties inherent in the construction of high-tension (4000, 10,000 volts) generators the current for ozone installations is usually derived from static transformers.

The static transformer may operate either on alternating current or on direct current with a suitable interrupter in the primary circuit.

(1) *Static Transformer with Alternating Current Generator.*

If a conductor such as a piece of wire describe simple harmonic motion in front of the pole of a magnet as is obtained in the rotation of an armature between the poles of a magnet, a current varying in intensity from moment to moment will be induced in the conductor.

Both E.M.F. and current time curves will follow those of the sine or cosine curve.

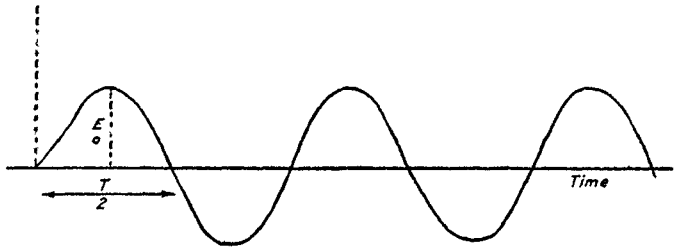

Fig. 7.

The E.M.F. at any time t being given by the relationship

$$E = E_o \cos \frac{2\pi t}{T}$$

the current in a similar manner by $i = i_o \times \sin \frac{2\pi t}{T}$.

If the circuit were entirely non-inductive, the volt-ampere curves would naturally be superimposed, since at any time the current flowing, would, in accordance with Ohm's law, be strictly proportional to the applied E.M.F. In actual practice self-induction is always present, being defined as the value of the integral—

$$L \iint \frac{\cos\theta \, dl \, dl'}{r}$$

where $\cos\theta dl\, dl'$ in the current circuit

The product Li may be termed the electrical momentum acquired by the current in the circuit, and Ohm's law has to be modified to include the rate of change of electrical momentum as well as the instantaneous current

$$\frac{d\left(\frac{Li}{dt}\right)}{dt} = E \cos \frac{2\pi t}{T} - Ri,$$

or

$$\frac{di}{dt} + \frac{R}{L} i = \frac{E}{L} \cos \frac{2\pi t}{T}.$$

The solution of this equation is given by

$$i = \frac{E \cos\left(\frac{2\pi t}{T} - \alpha\right)}{\sqrt{R^2 + \left(\frac{2\pi}{T}\right)^2 L^2}}$$

where $$\alpha = \tan^{-1} \frac{2\pi L}{RT}.$$

There is therefore a lag between the current and E.M.F. curves, and the maximum value of the current never exceeds $\frac{E}{\sqrt{R^2 + \left(\frac{2\pi}{T}\right)^2 L^2}}$ where the expression under the square root the "impedance" takes the place of R.

Several generalisations which have an important bearing on ozoniser designs follow from these considerations.

Firstly, large currents cannot be obtained in systems of high inductances, and with increasing values of the periodicity $\left(\frac{1}{T}\right)$ the inductance term becomes the only one of significance in the resistance of circuit.

For high frequencies $\frac{2\pi t L}{T}$ will be large, consequently augmenting tan a, making a the angle of lag approximately equal to $\frac{\pi}{2}$.

$$\therefore i = \frac{E_0 \sin \frac{2\pi t}{T}}{\sqrt{R^2 + \left(\frac{2\pi}{T}\right)^2 L^2}},$$

or when $\cos \frac{2\pi t}{T} = 0$, $\sin \frac{2\pi t}{T} = 1$, the E.M.F. will therefore be at a maximum when the current is zero and *vice versa*.

The Wattage consumption $E_0 i_0$ will be equal to

$$\frac{E_0^2 \cos \frac{2\pi t}{T} \cos\left(\frac{2\pi t}{T} - a\right)}{\sqrt{R^2 + L^2\left(\frac{2\pi}{T}\right)^2}} = 0 \text{ when } a \text{ is } \frac{\pi}{2},$$

or

$$\frac{\frac{1}{2}E_0^2 \cos a}{\sqrt{R^2 + L^2\left(\frac{2\pi}{T}\right)^2}} \text{ for small values of } a = \frac{\frac{1}{2}E_0^2 R}{R^2 + \left(\frac{2\pi}{T}\right)^2 L^2}.$$

For R = 0 or a there is therefore no energy consumption, whilst for some intermediate value there is a maximum energy consumption.

$$\text{For } \frac{R}{R^2 + \left(\frac{2\pi}{T}\right) L^2} \text{ to be a minimum}$$

$$R^2 \text{ must equal } \left(\frac{2\pi}{T}\right) L^2 \text{ or } R = \frac{2\pi L}{T}$$

If a condenser of capacity C be placed in circuit with the secondary system we can in a similar manner obtain the expression for the relationship between the varying potential difference and the charge on the plate.

$$Q = \frac{E\left(\cos\frac{2\pi t}{T} - a\right)}{\sqrt{\left(\frac{2\pi}{T}\right)^2 R^2 + \left(\frac{1}{C} - \frac{2\pi}{T} L\right)^2}}$$

By suitable adjustment of the condenser, i.e. making $C = \frac{T}{2\pi L}$, we can get larger amounts through the circuit for a given applied potential difference than if the circuit were closed by a wire.

According to Kalakjian ("Phys. Rev." 31, 117, 1910) the limiting yield of ozone increases with decreasing capacity,

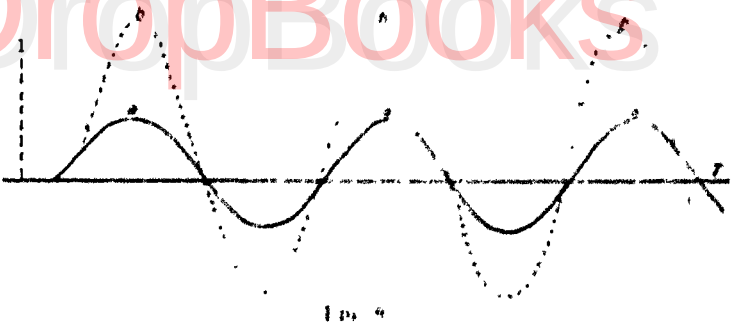

Fig. 9

whilst the efficiency of ozone production at a definite concentration increases with decreasing capacity.

So far we have assumed that the resistance R of the cir-

cuit is non-variant, but as we have had occasion to observe the conductivity of the air gap in the discharge apparatus varies with the current. Large currents cause the gap to become more conducting, permitting under a constant applied E.M.F. still higher currents to pass, ending finally in spark and arc discharges. The sinuous character of the curve will thus be altered, the maxima *a*, *a* being increased for this reason to higher values *b*, *b*.

(2) *Direct Current with Interrupter.*

Small coils with magnetic or larger induction apparatus, with mercury or Wehnelt type of make and break on the primary, also yield a periodic current which, however, no longer possesses the sinuous character of the alternating current machine, but consists of a number of periodic current makes and breaks as is depicted in the following curves :—

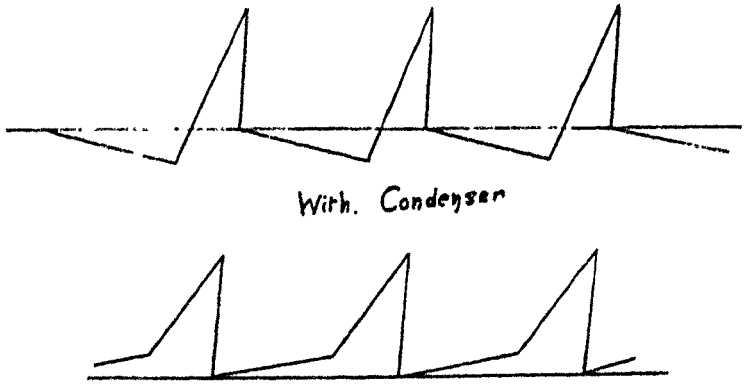

FIG. 9.

It will be noted that under both conditions of operation there exists a great danger of the spark discharge taking

place at the point of optimum current flow, which practically coincides with the period of maximum conductivity of the gas. The spark discharge itself is oscillatory in character having a period $T = 2\pi\sqrt{LC}$ and will present a curve of the following form :—

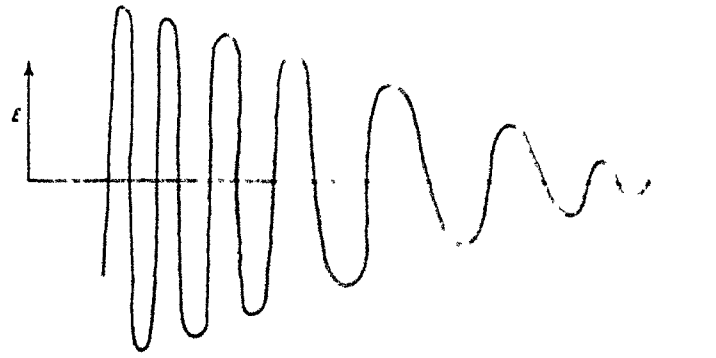

Fig. 10.

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According to the investigations of Kalckpan ("Phys. Rev.," 31, 117, 1910) the brush discharge itself may under conditions of high rates of discharge assume the oscillatory character of the spark discharge.

(*a*) *Influence on Voltage on Ozone Yield.* Chassy ("Etude sur l'Ozone, C.R.V.," 135, 1902) claimed that there was for a fixed air gap in a given ozoniser a practically linear relationship between the ozone yield per ampere hour and the potential difference between the electrodes. Later experiments have shown that Chassy's conclusions were not entirely correct. E. Warburg ("Ann. der Physik," 13, 464, 1904) showed that provided that the potential difference applied was sufficient to maintain a uniform glow at the point of the air gap, the yield of ozone was practically independent of the voltage as is shown by the following figures.

Current 1×10^{-6}.	*Voltage of Point.*	*Gms. Ozone per Coulomb.*
57	4,200	·0375
57·5	9,880	·0386
57·2	11,700	·0387

A. W. Gray ("Ann. der Physik," **13**, 477, 1904), utilising a standard Siemens ozoniser, likewise found that the yield per coulomb was constant and independent of the voltage provided that uniform illumination was maintained in the discharge space.

Kabakjian ("Phys. Rev.," V, **31**, 17, 1910) found that the ozone output per coulomb rapidly rose with the voltage until a potential difference of 2,700 volts with a 1 mm. air gap and 3,200 volts with a 2 mm. air gap was reached after which no further increase was noted. At these voltages presumably "saturation" of the field with the brush discharge was just effected.

Influence of Current Density.

With a constant regime established in the working of an ozoniser the quantity of ozone produced per coulomb is practically constant, for a point discharge on the other hand, the yield per coulomb varies with the current flowing, as is shown from the following figures obtained by Warburg:—

Positive Point.			*Negative Point and Positive Plate.*		*Negative Point and Positive Cylinder.*	
Voltage.	*Current* 1×10^{-6}.	*Grammes O_3 per Coulomb.*	*Current* 1×10^{-6}.	*Grammes O_3 per Coulomb.*	*Current* 1×10^{-6}.	*Grammes O_3 per Coulomb.*
8,420	28·8	0·0172	17·4	0·0489	—	0·0431
10,400	57·2	0·0600	25·1	0·0459	29·1	0·0386
12,000	94·2	0·0630	57·2	0·0375	94·2	0·0370

The variation in these figures is attributed by Warburg to the alteration in the volume of the current flow in the discharge space under the varying voltage. In a Siemens type of ozoniser operating under the optimum conditions, he obtained a value of 0·260 gms. per coulomb, a figure confirmed by A. W. Gray ("Ann. der Physik," 4, 177, 1901).

These figures show some light on the mechanism of ozone formation. Since, as can be shown by electrolytic decomposition or by measurement of the charge of the electron, together with the number of molecules in a gram molecule, 96,540 coulombs are associated with one equivalent of a substance, it necessarily follows that if the ozone were produced by some form of electrolytic action in the gas space, a limit is set to the quantity of ozone obtained per coulomb.

We may, of course, make various assumptions as to the magnitude of the electronic transfer associated with the formation of a molecule of ozone, but it will be evident that the maximum yield for the minimum transfer will be obtained on the assumption of the following possible sequence of reactions:

$$O_2 + 2O \rightarrow O + O$$

$$O_2 + O \rightarrow O_3$$

i.e. one molecule of ozone would be formed for each electron transferred. Forty-eight gms. of ozone should therefore be formed for a current consumption of 96,540 coulombs, or 0·0005 gms. per coulomb. It is evident that the quantities of ozone actually produced per coulomb exceed the amount some 520 times, even though these conditions represent those most favourable to ozone formation by electronic transfer.

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We are forced to the conclusion, assuming the accuracy of Warburg and Gray's experimental data, that most of the ozone is of secondary origin and is produced by collision between electrons both primary and secondary and gas molecules.

Krüger and Moeller ("Nernst Festschrift," 240, 1912) have suggested that one electron may liberate, in the case of the positive point discharge, seventeen secondary electrons, and for a silent discharge in metallic tubes 287 secondary electrons, which would necessitate velocities produced by applied voltages of approximately 100 and 50,000 volts respectively.

Influence of Wave Form.

The hypothesis advanced from the previous considerations that ozone formation is produced by inter-molecular and electronic collision, and is not a phase of gaseous electrolysis between the electrodes, is supported by a consideration of the effect of the wave form on the ozone yield. A. Vosmaer ("Ozone," Constable, 1916, p. 70) states, "a very peaked wave form would cause a greater distance between regular working tension and ordinary maximum tension and thus facilitate the brush discharge. On the other hand a flattened curve would give more available energy in the domain of working and would give a better output of ozone . . . there is not so much difference in wave form to be of any importance." It is clear that this investigator does not consider wave form of great importance and his views have been supported by many other observers. Those, however, who have had occasion to make use of the oscillograph and thus have been able to plot the wave form with accuracy have noticed

that the wave form does have an important bearing on the yield of ozone. Amongst the more important investigations published, may be mentioned those of O. Fröhlich ("Elektrotech. Zeitschrift," **12**, 340, 1901). E. Warburg and Leithäuser ("Ann. der Physik," **4**, 28, 17, 1905), and G. Lachmer ("Zeit. Elektrochem.," **17**, 114, 1911; **21**, 309, 1915).

The following is a brief summary of the more important conclusions:

The ozone yield per coulomb rises at first rapidly with the periodicity of the alternating current and thereafter more slowly. Up to 500 periods have actually been employed in technical installations. It is evident from a consideration of the form of the sine curve that an increasing periodicity increases the steepness of the curve, i.e. high periodicity causes a large value for the rate of alteration of the current flow $\frac{di}{dt}$. A high periodicity likewise lowers the minimum potential difference to produce a silent discharge across a fixed interpolar space (E. Riesenfeld, "Nernst Festschrift," 371, 1912).

More ozone is produced per coulomb with a periodically broken direct current than with an alternating current of the same current strength and periodicity. A glance at the typical wave forms for these two types of current flow will suffice to indicate that in the former case the $\frac{di}{dt}$ values are much larger than in the symmetric alternating currents. A further advantage of the direct current is that for the same effective potential difference a larger current can be passed through the silent discharge tube with a consequent increase in ozone production.

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Plaschin and Kauchtschev ("J. Russ. Phys. Chem. Soc.," 46, 576, 1914) have likewise shown that the yield of ozone increases with the frequency, but that the optimum frequency was dependent on the applied voltage as indicated by the following figures:—

Periodicity.	*Applied Voltage.*
1240	6500
950	7000
660	8000

For a constant air-flow an increase in periodicity above these limits decreases the output of ozone, whilst an increasing air-flow displaces the maximum towards increasing frequencies.

In a general way it is not difficult to offer an explanation of the increase in yield of ozone per coulomb with rapid alteration of the current flow or increasing tension of a current impulse, if we regard the formation of ozone due to electronic and molecular collisions.

At any given instant we may regard the current flow as constant; then proceeding from the negative to the positive electrode there will be a stream of electrons which, in their passage through the gas space will ionise part of the gas therein. The effect of the electron stream on the oxygen fraction of the gas is three-fold:—

(*a*) A splitting of the molecule into two neutral atoms by direct impact—

$$O_2 = O + O.$$

As we have seen it is by this disruption that ozone is chiefly formed in ultra-violet light.

(*b*) An ionisation of the molecule or atom by impact—

$$O + O_2 + e'$$

$$O + O_2$$

the positive ions so formed which may be at once or exist of molecule clusters (we have already indicated that evidence for clusters up to O_6 in complexity is at hand, this probably represents the extreme upper limit, a large cluster easily break down again). The atoms or molecules with one or two positive charges naturally proceed in the reverse direction to the stream of electrons and by impact and combination with them neutralisation to atoms and molecular groups is once more effected.

$$O_2 + 2' \quad O_2$$

(*c*) An ionisation of the molecules or atoms by impact and adherence of the electron.

The electron having spent most of its kinetic energy with which it left the electrode or dielectric, may, on contact with a neutral atom or molecule, not possess sufficient energy to detach a valency electron from its orbit of rotation and may actually adhere to the system at rest, forming a negatively charged atom or molecule.

$$O + \quad \cdots O_2$$

$$O + \cdot \quad - O$$

Oppositely charged atoms and molecules may then react to form ozone.

$$O_2 + O^- \cdot \quad O_3$$

If the current flux be subject to violent changes then the stream density of both electrons and gas molecules will not be constant, but will proceed by a succession of irregular spasmodic bursts of varying velocities, thus greatly enhancing the possibilities of collision.

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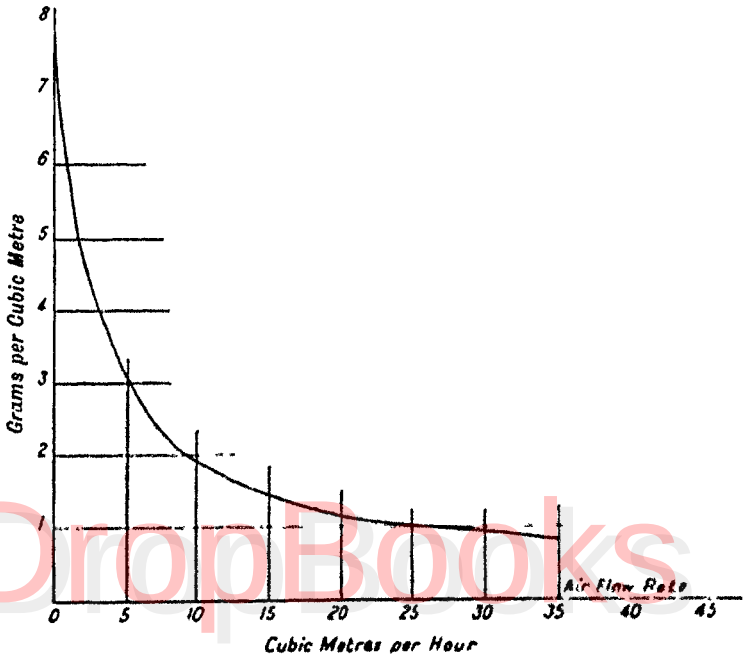
Influence of Gas Flow and Composition.

We have already referred to the fact that the output of an ozoniser is governed by the concentration of the ozone formed during the discharge, since for high concentrations the rate of deozonisation is increased and the apparent yield of ozone per kw. hr. decreased. In the curves on next page are shown the relationships obtained between yield and concentration by utilising a standard Siemens and Halske industrial ozoniser (Erlwin, "Zeit. f. Sauerstoff and Stickstoff," 6, 143, 1911).

Warburg and Leithauser ("Drud. Ann.," 28, 1, 1908) made a very extensive series of experiments on both glass and metallic ozonisers to determine the influence of the ozone concentration derived upon the yield. Their results are tabulated in the following columns:—

Type of Ozoniser.	*Distance between Electrodes in Cms.*	*Voltage.*	*Periodicity.*	*Amperes.*	*Cos θ.*	*Gms. per Ampere Hour for Concentrations of Gms. per Cubic Metre.*		*Limiting*	
						10	4	*Yield Gms./Amp. Hr.*	*Concentration in Gms. per Cubic Metre.*
Glass	0·51	8,050	50	0·182	0·185	38·3	41·9	45·5	3·5
"	1·40	10,080	50	0·102	0·314	—	—	—	—
"	1·40	16,900	50	0·193	0·243	52·3	55·1	56·8	50·2
"	3·72	17,500	50	0·160	0·415	51·1	56·1	60·1	31·2
Metal	2·26	10,800	50	0·182	0·431	72·2	78·4	82·6	40·5
"	4·66	13,900	50	0·169	0·450	53·3	62·4	68·4	20·2
"	2·26	9,480	100	0·308	0·451	75·7	81·4	88·2	51·6
"	4·66	12,300	100	0·280	0·447	54·0	63·0	69·0	16·8
"	2·26	9,340	510	1·58	0·537	57·1	66·0	71·9	18·3
"	4·66	12,100	510	1·19	0·704	33·0	58·0	74·7	11·4



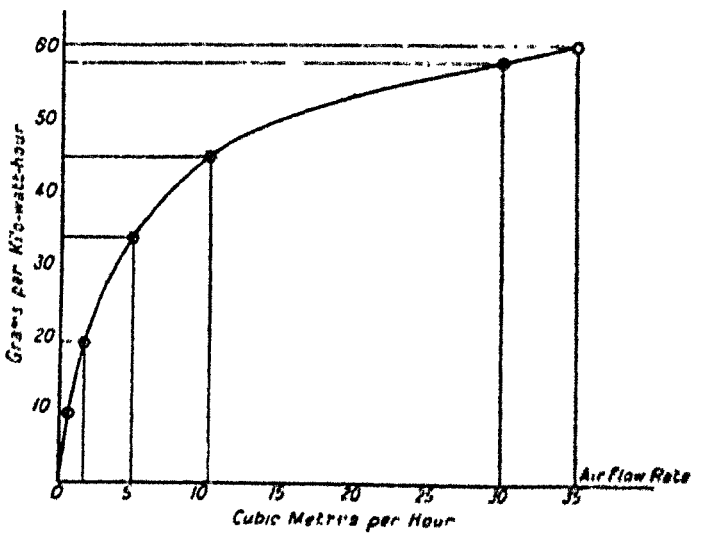


FIG. 11.

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It will be noticed that the conditions most favourable for the economic production of ozone obtain with low concentrations of ozone or relatively high flow rate of air. High air flow rates likewise serve to keep the ozoniser cool, an important consideration since the catalytic decomposition of ozone is considerably accelerated by high temperatures.

For technical operations the air-flow rates are accordingly adjusted as to give the minimum concentration of ozone which will prove effective for the process under consideration; for under these conditions, although more energy must be expended for pumping air, yet a very considerable economy is effected in the ozone production.

The concentrations of ozone and the yields obtainable per kw. hr. are higher in oxygen than in air, but the employment of oxygen instead of air does not prove to be economical in practice, although concentrations up to 150 gms. per cubic metre, or nearly three times the maximum concentration attainable with air, can be carried out.

The yield, however, does not increase indefinitely with the oxygen pressure, thus, H. von Wartenberg and L. Max ("Zeit. f. Elektrochem.," **14**, 879, 1913), operating with an ozoniser constructed to withstand high pressures with an interpolar space of from 2 to 6 mm. and a current of 1 milliampere at 23,000 volts and 50 periods, obtained the maximum ozone concentration and ozone yield per watt-second at 0·5 to 1 atmosphere. Pressures up to 5 atmospheres were reached during the course of their experiments.

It will be noted that 60 gms. of O_3 in air, and 180 gms. of ozone in oxygen per kw. hr. represent the best results yet obtained with ozonisers operating under the optimum

conditions. Taking 34,000 calories as the heat of formation of ozone, this represents a theoretical yield of 1·2 kgms. per kw. hr., or industrial ozonisers have an efficiency of only 5 per cent. in air or 15 per cent. in oxygen.

Air suitable for ozonisation should be free from dust, which favours the passage of sparks, and from certain gaseous impurities such as oxides of nitrogen, chlorine, and more especially water vapour. All three gases appear to exert a distinct inhibiting effect on the formation of ozone, in addition to a deozonising action, which is especially marked in the case of chlorine and nitrogen dioxide. The function of these gases as catalytic deozonisers will be referred to later. The inhibiting action, which is most marked in the case of water vapour, has been attributed to the formation of mist, which serve as nuclei for the condensation of the gas ions. Under these conditions of condensation, the velocity of the ions is naturally reduced and their power of ionising or breaking down a molecule into atoms is correspondingly lowered. Undried air at ordinary temperatures having a water vapour pressure of ca. 7mm H_2O has a limiting yield of ozone which is only 60 to 70 per cent. of the air when dry; in the presence of moisture likewise the formation of oxides of nitrogen, due to the thermal effects of sparking as well as the possible interaction of ozone with some form of active nitrogen produced in the spark discharge, is usually occasioned. T. Lowry ("J.C.S.," 101, 1152, 1912), in an interesting research on the effect of the silent and spark discharges on air, showed that in dry air oxides of nitrogen were not formed under the experimental conditions by passage through the ozoniser or the spark discharge gaps. When

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passed, however, through both in series, or when the air currents subjected to each discharge were mixed, oxides of nitrogen were produced.

Lowry came to the conclusion that in the spark discharge an active variety of nitrogen was formed which was easily oxidised by ozone.

Dielectric Material.

We have already noted that the yield of ozone per kw. hr. at a definite concentration increases with the increase in capacity of the ozoniser, but that the limiting yield decreases. In addition it must be remembered that extreme variation in the size of the air gap or interpolar free space is not permissible, since too small a gap will permit the passage of sparks and possible arcing with minute variations in the applied voltage, whilst with a large interpolar free space the luminous discharge, on which the formation of ozone appears to be largely dependent, will not fill or "saturate" the field. It is evident that the use of dielectric material other than air, by which alterations in the capacity and interpolar distances can readily be made, offers the designers of ozonisers a very considerable latitude in these factors.

For the purposes of calculation we may take a simple plate form of ozoniser and consider the effect of inserting a plate of dielectric material in the air space between the two metallic electrodes.

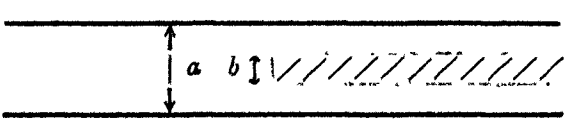

Fig. 12.

If the two plates are charged with a quantity of electricity of surface density σ, the attraction, at a point P situate in one plate, by the other plate which is separated from it by the interpolar distance (a) is—

$$F = \int_a^a \frac{2\pi r dr\sigma \cos\theta}{a^2 \sec^2\theta} = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{2\pi R \tan\theta \sigma Q \sec^2\theta d\theta \cos\theta}{a^2 \sec^2}$$

$$= \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} 2\pi\sigma \sin\theta = 2\pi\sigma.$$

At a point between the two plates the attraction due to each plate is $2\pi\sigma$, thus, with a positive charge on one plate and a negative charge on the other, $F = 4\pi\sigma$.

If the potential difference be V, and the total charge Q, then $\frac{V}{a} = 4\pi\sigma = \frac{4\pi Q}{A}$, A being the area of each plate, or the capacity $= \frac{Q}{V} = \frac{A}{4\pi a}$,

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if we neglect the irregular distribution of the stream lines near the edges of the plates.

On the insertion of a piece of plate glass of thickness b between the plates, the equivalent air thickness is $\frac{b}{K}$, where K is the specific inductive capacity of the glass, hence the new capacity will be augmented to $\frac{Q}{V} = \frac{A}{4\pi\left(a - \frac{b}{K}\right)}$, and the interpolar distance of air space reduced to $a - b$. By this means we have augmented the capacity and decreased the interpolar distance of the ozoniser, and thus increased its efficiency; at the same time the tendency to sparking and rupture of the gap between the electrodes is diminished, since the mechanical force per unit area is likewise reduced, and

the possibility of the flow of currents of high densities naturally excluded.

The following are the approximate values of the specific inductive capacities of the more common dielectric materials, dry air being taken as unity :—

Material.	*K.*
Paraffin wax	2·3
Rosin	2·6
Ebonite	3·2
Sulphur	3·8
Glass	6 to 7

The choice of dielectric material is naturally limited, since it has to withstand both high temperatures and the destructive oxidising action of the ozone. Amongst those which have been suggested may be mentioned: shellac, mica, quartz, glass, and artificial insulators formed by condensation of phenol and formaldehyde, the so-called Baekelites; glass, however, is the only material which has received extended technical application.

The effect of insertion of a solid dielectric in the interpolar space is, however, not so simple as indicated by the above considerations, since like other materials, not only are they imperfect insulators, but many of them possess the interesting property of acquiring residual charges. We may regard the dielectric medium to consist of a number of conducting particles embedded in an insulating material, the fraction being smaller in the case of the more perfect insulators. If this fraction be denoted by u, then the specific inductive capacity can be calculated approximately from the relationship :—

$$K = \frac{1 + 2u}{1 - u}$$

u being determined from the molecular specific volume $\frac{u}{d}$.

When a strip of dielectric material is charged up to a high potential, after discharge it will be found to acquire a small charge on standing, which is often sufficiently great to raise the potential of the dielectric up to 300 volts. This property of acquiring a residual charge is only possessed by those bodies which possess the property of exhibiting elastic after-effects, it is never shown by simple substances, but only by mixtures such as the glasses; thus xylene and paraffin oil alone do not show this effect, but on mixing the two, the residual charge is apparent. One of the constituents must also possess a certain amount of electrical conductivity.

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It is interesting to note that Riesenfeld ("Zeit. Elektrochem.," 725, 1911) failed to obtain a brush discharge with pure quartz glass, although such discharges are readily obtained with all forms of glass which may contain quite large percentages of silica, attributable to the slight electrical conductivity of the glass, and its possession of a residual charge.

Two other important properties of dielectric materials must be briefly alluded to, namely, the alteration in conductivity with elevation of the temperature, and the modification which the dielectric undergoes when subjected to electrical stress.

It is well known that the conductivity of glass at even slightly elevated temperatures rapidly increases. Mond and Langer and Huber have actually used solid glasses as electrolytes at temperatures between 200° and 500° C. Local

overheating at one point in the dielectric, due to a slight irregularity in the current flow, will thus cause an increase of conductivity at this point, with a corresponding augmentation of the current. Fusion and finally perforation of the glass results. It is for this reason that porcelains, which possess temperature coefficients even higher than those of the glasses, are unsuitable for dielectric material in ozonisers.

Kerr noted that the optical properties of dielectrics were considerably modified by the application of electric stresses. These modifications are influenced by the period of time for which the stress has been applied, thus Fleming (see "Amer. Suppl.," 45, 1912) showed that the conductivity of a dielectric varied with the frequency of the applied alternating current, and Lipp ("Hochspanning Technik") found that the applied voltages necessary for perforation of thin sheets of dielectric material varied with the period to which the dielectric material had been subjected to the electrical stress. The perforating potentials for the usual dielectric materials are approximately as follows:—

Material.	*Perforating Potentials in Kilovolts per Cm.*
Mica	600 to 750
Micanite	400 „ 500
Porcelain	100
Glass	75 „ 300
Lead glass	1000

Air ("Amaduzzi N. Cimenta," 3, 51, 1912)—

7000 volts per 1·5 cm.
97,000 „ „ 13·5 „
100,000 „ „ 14 „

The potential difference necessary for discharge between two conductors in air varies with the size and shape of the

conductor, point discharge taking place much more readily than discharge across plane surfaces. The following figures (Abraham and Villard, "Physical Constants," 1910) indicate the potential difference required to cause a 30 mm. spark to strike between two spherical electrodes of varying radius :-

Radius in Mm.	*Potential Difference.*
∞ (plane)	82,700
300	85,100
100	81,100
50	90,000
0 (point)	30,300

The relationship between the potential difference and the striking distance, is also not a simple one, as indicated from the experimentally derived figures for spherical electrodes 1 cm. in radius :-

Distance in Cms.	*Kilovolts.*
0·05	27
0·10	41
0·40	13·0
0·50	13·6

For very small interpolar distances, say 1 to 50 $\mu\mu$, the voltage necessary is independent of the distance and equal to about 350 volts (E. Williams, "Phys. Chem.," **31**, 216, 1910).

O. Hoveda ("Phys. Rev.," **34**, 25, 1912) gives the following relationship for point to plane discharges :-

$$V = a + \frac{b}{c + \sqrt{D}}$$

where a, b, c, are constants, and D is the interpolar distance.

The use of minute points corrugated or roughened metal electrodes in industrial ozonisers is very frequent, since, as we have seen, the presence of points facilitates the electrical discharge.

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L. Décombe ("Jour. de Physique," **2**, 181, 1912) has attempted to calculate the energy dissipated in a condenser when connected to an alternating current source; he shows that the energy absorbed, i.e. $V\delta q$ (where V is the applied E.M.F. and q the charge on the condenser), can be expressed in the form :—

$$V\delta m + R_0\delta V,$$

where m is the polarisation and R_0 a constant, this is equivalent to the dissipated energy :—

$$= \int_0^T \nabla\delta m = \int_0^T V \left(\frac{\delta m}{dt}\right)^2 dt,$$

or the dissipated energy is proportional to the square of the polarisation current and independent of the periodicity. V. Ehrlich and F. Russ ("Zeit. Elektrochem.," **19**, 330, 1913), as a result of an investigation on the measurement of the electrical quantities in a Siemens ozone tube, showed that the ionisation or polarisation current and applied potential were always in phase, and that the potential difference across the gas gap was a direct measure of the energy.

Chassy ("Jour. de Physique," **2**, 876, 1912), on the other hand, showed that the energy absorbed per second by a gas under alternating fields, varied as the charge Q and not as the square of the charge, as in metallic conductors.

An increase in conductivity of the solid dielectric is also to be expected from its exposure to the ultra-violet light generated by the brush discharge in the interpolar air gap. A. Goldmann ("Ann. der Physik," **36**, 3584, 1911) has shown that solid dielectrics exhibit both an increase in conductivity and a negative discharge of electrons similar to the Hallwachs effect in metals when subjected to ultra-violet

irradiation; the conductivity of sulphur is said to increase 1500 times when thus illuminated.

Types of Industrial Ozonisers.

Industrial ozonisers may be grouped into two distinct types: those in which the silent discharge passes across the air gap without the interposition of any solid dielectric, and those in which one or both of the electrodes are protected by some suitable dielectric material, usually glass.

Non-dielectric Ozonisers.

Several attempts have been made to produce an ozoniser without any dielectric and although large units on various systems have been constructed from time to time, their efficiency has usually been extremely low and at the present time all industrial ozonisers contain dielectric material.

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Schneller, Wisse and Sloen, in 1894, were the first to construct large ozonisers without a dielectric. One discharging surface consisted of a sheet of platinum gauze to provide a great number of small points some 30 mm. from the other surface formed of perforated metal sheet, the air current being forced through the perforations in the sheet. The two electrodes were cylindrical in shape and were mounted in glass tubes. The operating voltage was at first 15,000, which was subsequently raised to 50,000. To avoid the formation of an arc discharge, which in the absence of any dielectric between the electrodes would be attended with disastrous effects, a high resistance was inserted in series with the ozoniser.

These investigators found much difficulty in the construction of a resistance suitable for the purpose. It was

necessary to obtain a suitable resistance of 1·5 megohms, capable of carrying 0·01 ampere; moist unglazed porcelain and glass tubes containing 80 per cent. glycerine were found most suitable. Vosmaer ("Ozone," p. 94) showed that sparking and arcing could not be avoided even with this artifice, and that the external resistance served to increase the capacity of the circuit rather than the resistance.

Slate was found to be more suitable than either glycerine or moist unglazed porcelain, which rapidly lost its humidity and suffered an increase in resistance.

Patin's ozoniser followed a similar construction; refrigeration of the air prior to ozonisation was employed to increase the yield, and a number of small metallic perforated prisms enclosed in a single unit comprised the electrodes in lieu of the perforated plates and gauzes in Schneller's apparatus.

Various improvements in design of this type of ozoniser were introduced by Tindal in 1894 and more especially by De Frise in 1904. De Frise's plant was actually employed for a short period in the sterilisation of water on a large scale at the Saint-Maur Water Works at Paris, but the dielectric Siemens-Halske ozoniser was subsequently installed and adopted as proving itself more economical in operation.

Tindal employed Schneller's method of augmenting the capacity of the system by the insertion of liquid resistances in series with the ozoniser. The ozoniser consisted essentially of a system of compartments separated by perforated metal plates, containing alternately a set of electrodes and a water-cooling device.

The perforated metal plates attached to the cooling tubes served as one set of electrodes of the ozoniser and fine gauze as the other set.

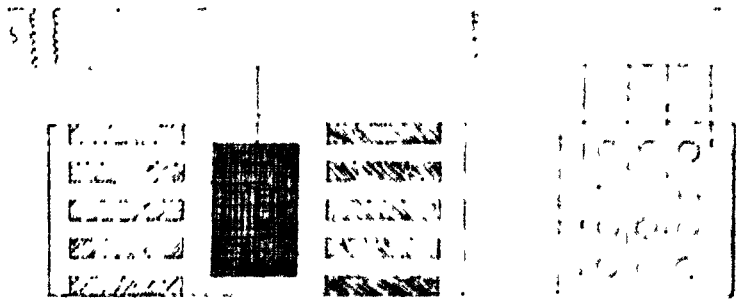

Fig. 10.

The water was maintained in active circulation to augment the cooling.

De Frise likewise adopted Tindal's arrangement of alternating ozonisation and refrigeration, but adopted a different arrangement for the distribution of the electrodes.

These consisted essentially of a series of crescent-shaped discs mounted in parallel each with its own liquid inductive capacity in a water-cooled metallic trough which served as the other electrode.

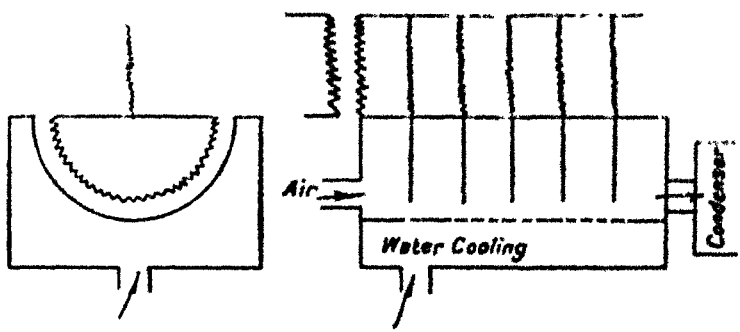

Fig. 11.

Each disc was furnished with a number of minute points to facilitate the discharge.

These ozonisers were in successful operation with voltages up to 10,000, although an applied voltage of from 15,000 to 20,000 was usually employed.

It possessed distinct advantages over Tindal's apparatus in that the distance between the electrodes could be reduced very considerably without risk of arcing, thus increasing the efficiency of the apparatus.

Various types of mechanical ozonisers operating without the interposition of any dielectric have been constructed from time to time, the most successful being that of Otto.

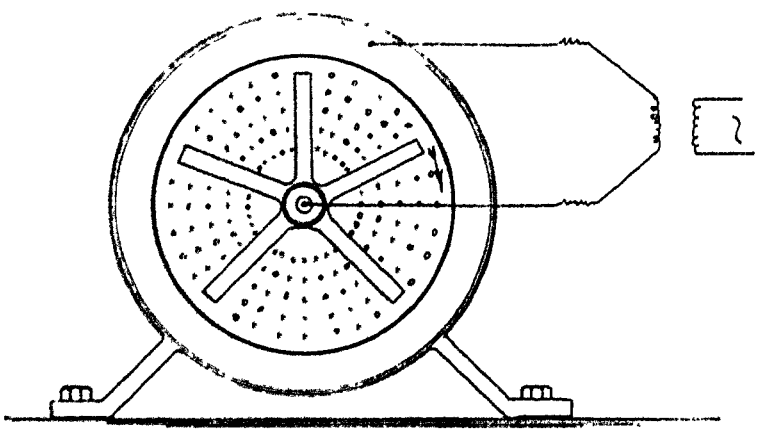

FIG. 15.

The frequent occurrence of arcing in non-dielectric ozonisers as well as the necessity for obtaining a very small polar distance between the electrodes for efficient working, led Otto to construct an ozoniser in which by the rotation of one electrode the polar distance was always varying, so that if for any accidental cause an arc should be formed at one

point, it would speedily be broken again by the subsequent increase in the arc gap. A diagram of an improved form of Otto ozoniser is shown above. One electrode, which is fixed, consists essentially of an aluminium disc, studded with a great number of small points, the rotor being a metallic disc segmented with insulating material. Up to 80,000 volts have been employed on these machines.

None of these ozonisers have proved sufficiently economical or reliable for industrial operations in which, at the present time, ozonisers containing one or more dielectrics are practically universally employed.

Ozonisers Containing a Dielectric.

Tubular Ozonisers.—The present construction of serviceable apparatus for the production of ozone by means of the silent discharge has developed from the simplest forms of ozone tubes constructed by von Siemens, in 1857, in Germany, by Brodie in England, and Berthelot in France.

Siemens' first ozoniser consisted essentially of two coaxial glass tubes, the outer coated externally and the inner internally with tin-foil, the air being passed through the annular space. Brodie substituted water as electrode material in the place of tin-foil, and Berthelot used sulphuric acid

These ozonisers thus contained two dielectric plates covering each electrode, and in practice gave serviceable and uniform results.

Brodie's and Berthelot's system gives somewhat better results than that of Siemens', since it is a simple matter in these forms to arrange for efficient cooling of the electrodes and interpolar space. When oxygen is employed instead of

air, a 10 per cent. ozone concentration can easily be obtained at room temperature and over 20 per cent. at −25° C.

Yet another type of apparatus was introduced by Dr. Oudin and Andréoli in 1893. As one electrode a simple form of glass vacuum tube was used, electrical connection being furnished by means of a sealed-in platinum wire, which in Andréoli's apparatus ran through the whole length of the tube. The second electrode consisted of a series of equally spaced indented steel rings, surrounding the vacuum tube, or a copper spiral coiled in the form of a helix round the tube; the whole unit being inserted in a glass tube through which the current of air was passed. Gaiffe and E. Chatelain at a later date modified Oudin and Andréoli's apparatus by substituting a second annular vacuum tube in place of the steel or copper electrode by the former investigators.

Small types of Oudin and Andréoli's machines were at one time popular for medical work but have not been developed for industrial purposes.

The Siemens type of ozoniser was developed by Fröhlich and Erlwein, of Siemens and Halske, to its present form, which has proved to be eminently suitable for industrial purposes.

The tubular form of the earlier form of apparatus was preserved, but various modifications were made in the disposition of the electrodes.

For the internal tin-foil coated glass tube, a cylindrical aluminium tube was substituted, maintained in position in the outer tube (of glass), and separated from it by 1·5 mm. by means of three ebonite spring plungers. As the other

electrode, Brodie's idea of using water was adopted and provision was made for circulation to ensure cooling, the cast-iron frame containing the ozoniser and water cooling being carefully earthed. The smallest technical unit contains two ozone tubes, the largest eight in the same water-cooling frame, which is provided with a glass inspection plate. The operating voltage varies between 4000 and 10,000 volts.

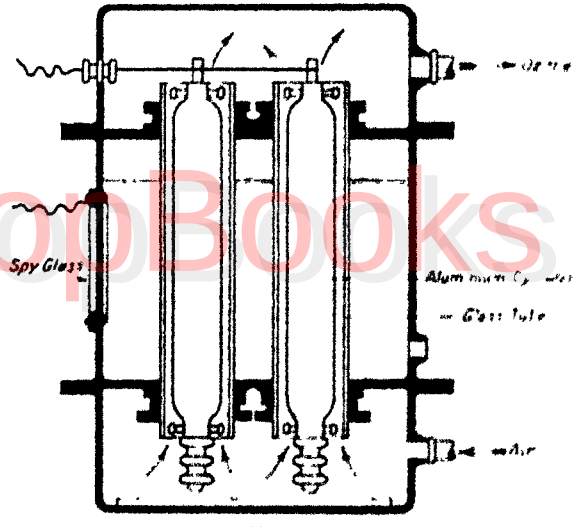

FIG. 16.

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We have already discussed the results obtained by Erlwein with this type of apparatus and will refer to the technical applications in a subsequent section.

A similar type of apparatus has been developed by the General Electric Company, but the somewhat cheaper and equally efficient enamelled iron has been substituted for the aluminium.

The Westinghouse Company in the Gerard ozoniser sub-

stitute oil for water as the external electrode, and utilise, as in the early Brodie tube, a double dielectric system.

According to the investigations of Vosmaer, the economical production of high concentrations of ozone is realisable in this type of apparatus.

Various other forms of tubular ozonisers have been the subject of patent literature, a few of which, such as the

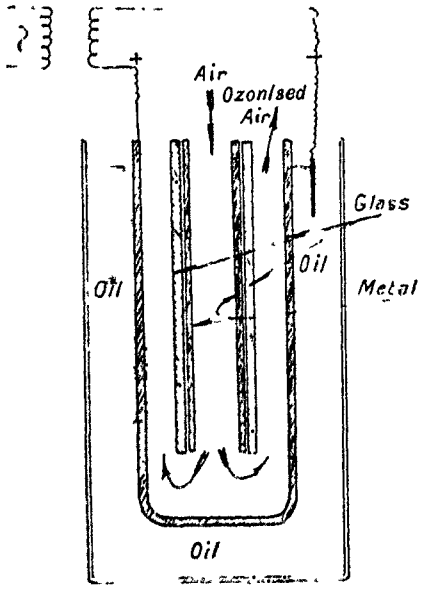

FIG. 17.

Elworthy, Yarnold and Gaiffe, have been sporadically developed for a short time by small companies, only to sink again into oblivion. In Europe the only representation of this type of ozoniser which may be said to have established its footing industrially is that of Siemens and Halske.

Plate Type Ozonisers.—In the tubular type of ozoniser, owing to the disposition of the electrodes, it would appear

that the use of cooling water is essential in order to keep the interpolar space and the inner electrode relatively cool, which, as we have seen, is one of the most important factors in the economic production of ozone. Since the thermal radiation obtainable from two parallel plates is much greater than in the tubular form, where the radiation is practically confined to the interpolar area and to the external surface of one electrode, the provision of cooling water is not essential for efficient operation. Although better results are obtainable in well-designed ozonisers, where water cooling is used in addition to the cooling effected by the air passage, yet with air-cooled plate ozonisers of the proper design and with the enhanced capital and running costs entailed in water-cooling devices, the cost of ozone production by either method is approximately equal. Nevertheless, in those cases, usually exceptional, where high ozone concentrations or low air current velocities are required, provision for water would appear desirable. Modern plate form ozonisers have consequently developed on these two distinct lines, those in which air cooling only is utilised and those in which supplementary water cooling is made use of.

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Air-cooled Plate Ozonisers. The earlier ozonisers of this type, such as those of Villon and Genin of Prépoignot, and an experimental one of Otto's, were not a success, since it was found impossible to prevent a very considerable rise in temperature during continuous operation, resulting in a serious loss of efficiency.

The first technical ozoniser which showed promise was that of Andréoli, and possessed the great merits of simplicity of construction and uniformity in operation.

Andréoli's ozoniser consisted of a series of serrated aluminium plates separated from each other by a sheet of glass, ca. 2 mm. thick, and an air gap. Each plate had an area of 30·5 × 30·5 cms., and possessed 17,760 points formed by indentation of the serrations. These units were mounted in a wooden box; provision was made for possible expansion and contraction, and various artifices were devised to ensure the plates being inserted quite parallel with each other.

With an eight-plate ozoniser, operating with a voltage as low as 3,300 volts, an energy consumption of 550 watts could easily be maintained, producing ca. 60 to 100 gms. of ozone per kw. hr., naturally at very low concentrations. In his later models Andréoli likewise introduced water cooling, and could consequently elevate to applied voltage from 3,300 to 10,000, without any undue rise in temperature.

Experimental ozonisers of similar construction have been designed by Vohr and Vosmaer but do not appear to have been developed for industrial purposes. The only air-cooled type plate ozoniser which appears to have outgrown the experimental state, and to be actually employed in the various industries, is that of the Ozonair Company.

This ozoniser is extremely simple in construction and efficient in operation. The electrodic discharge through the glass dielectric plates and air gap is facilitated by employing flat sheets of metallic aluminium alloy gauze as electrode material; this possesses the dual advantage of an even distribution of points over the whole electrode area, and of being practically resistant to corrosion or tarnishing. Cooling is effected by the air current and concentrations up to 3, and, for short periods, even 4 gms. of ozone per cubic metre may be

obtained under conditions of actual operation without undue elevation of the temperature. The operating voltage is usually 5000 at periodicities varying from 25 to 100. Tests have shown that at a concentration of 2 gms. per cubic metre the output may exceed 100 gms. per kw. hr.

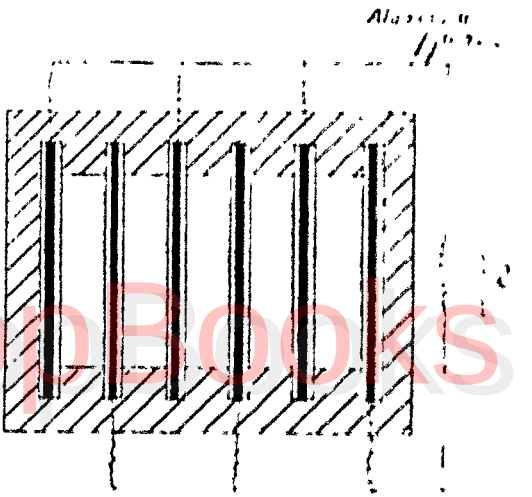

FIG. 18.

Water-Cooled Plate Ozonisers. This type of ozoniser was developed chiefly by the early investigations of Otto, and subsequently by those of Marmier and Abraham; as a result the Otto Marmier Abraham Ozoniser was constructed, which has found a by no means insignificant number of industrial applications, especially in France.

The unit consists of a pair of hollow disc electrodes with perfectly plain faces which are protected by plates of the dielectric, in this case glass, some 2 mm. thick. The inter-polar air space through which the air flows in a radial direction varies from 13 to 18 mm. in width. Each electrode

is cooled by running water, a broken fall providing against short circuiting through the earth.

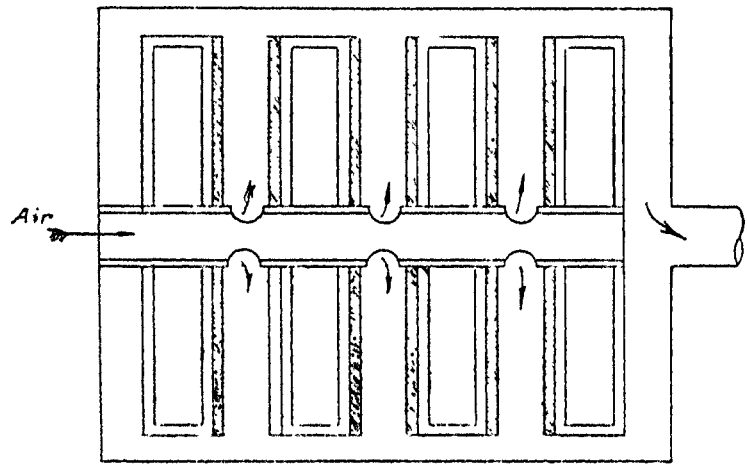

FIG. 19.

The outer casing is made of earthenware, the air being forced in at one end and emerging after ozonisation at the other.

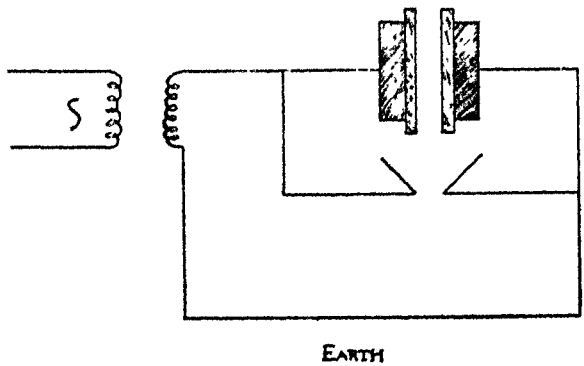

FIG. 20.

The ozoniser operates successfully at a voltage of 30,000 to 40,000 volts, although voltages much lower than this can naturally be employed, 12,000 being quite normal.

Otto introduced for these machines a simple form of electric safety valve consisting of two horn-shaped electrodes, separated by a variable air gap and placed in series with the ozoniser.

An accidental rise in the operating voltage would cause a discharge to take place across the air gap when suitably adjusted, and thus obviate any breakdown in the dielectric plates of the ozoniser.

Labille suggested the use of mica as a dielectric in place of glass plate in ozonisers of this type, but in practice, owing to the disintegration of this laminated material, unfavourable results were obtained.

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CHAPTER VIII.

THE CATALYTIC DECOMPOSITION OF OZONE.

SINCE the quantity of ozone in equilibrium with atmospheric oxygen at ordinary temperatures is, as we have seen, almost vanishingly small, it follows that in ozonised oxygen or ozonised air conditions of unstable equilibrium obtain, and the apparent stability of the ozone is due to the fact that the equilibrium is "frozen," or the rate of decomposition of ozone at these temperatures is almost negligible. The rate of decomposition of the ozone in excess of the minute amount present at the true equilibrium can be accelerated in a variety of ways, such as by the addition of catalytic materials, either solid, liquid, or gaseous, by photo-chemical action, or by purely thermal methods, by slightly elevating the temperature.

The rate of decomposition of ozone has been the subject of many investigations. Shenstone in 1897 considered dry ozone to be extremely unstable, and to undergo decomposition with extreme rapidity. At a later period, H. E. Armstrong showed that, in the absence of oxides of nitrogen, the rate of decomposition was sensibly lessened.

Jahn ("Zeit. Anorg. Chem.," 48, 260, 1906), at Nernst's suggestion, conducted a series of experiments on the rate of decomposition with a view to elucidating the mechanism of decomposition. The ozone molecule may undergo

decomposition in a variety of ways, as indicated in the following equations:

(i) $2O \rightarrow O_2$

(ii) $O_3 \rightarrow O_2 + O$

(iii) $O_3 + O \rightarrow 2O_2$

Jahn's experimental results appeared to indicate that the rate of decomposition could be formulated in the expression

$$\frac{d\epsilon(O_3)}{dt} = K\frac{(C(O_3)^2}{C(O_2)^3}.$$

He consequently argued that the decomposition followed the course indicated by equations (ii) and (iii), on the assumption that the first reaction was rapid and reversible

$$O_3 \rightleftarrows O_2 + O,$$

and the second slow and irreversible

$$O_3 + O \rightarrow 2O_2.$$

Perman and Greaves ("Proc. Roy. Soc.," **4**, 807, 354, 1908) likewise stated that the rate of decomposition was inversely proportional to the concentration of the oxygen

$$\frac{d\epsilon(O_3)}{dt} = \frac{K}{C(O_2)}$$

Chapman and Clark ("Trans. Chem. Soc.," **93**, 1638, 1908) and Chapman and Jones ("Trans," **254**, 2163, 1910) subjected the whole matter to an exhaustive examination, they showed that Jahn's and Perman's interpretation was not correct and that very serious errors due to the catalytic effect of the surface of the glass vessel vitiated the accuracy of their results. These investigators found that the rate of decomposition was proportional to the square of the concentration of the ozone and independent of the oxygen pressure;

or $$\frac{dc(O_3)}{dt} = KC(O_3)^2.$$

E. Weigert ("Zeit. Phys. Chem.," 80, 78, 1912), however, obtained values corresponding to an order of decomposition somewhat exceeding two in the dark.

The rate of decomposition is greatly accelerated by rise in temperature, being almost instantaneous at 270° C. and quite rapid at 100° C. This fact, namely, that the equilibrium is not to be regarded as "frozen" until room temperatures are arrived at is, as we have seen, the factor militating against the successful thermal production of ozone in contradistinction to nitric oxide where the equilibrium is practically "frozen" at 600° C.

The decomposition may likewise be accelerated by solid catalytic agents such as the following:—

Ag, Cu, Co, Ni, Cr_2O_3, Pb_3O_4, V_2O_5, MnO_2, TiO_2, ThO_2, CeO_2, U_3O_8, W_2O_3, BaO, CaO, Hg, Ni, Pt, Pd, V, and powdered glass.

The catalytic activity of platinum black is extremely great. Mulder and v. d. Meulen ("Rec. Trans. Chem. Pays.-Bas.," 1, 167) and Warburg ("Berl. Akad., Ber.," 1, 1900, 1176, 1901) noted the rapidity of decomposition of ozone rich gas when passed over cold or warm platinum black, whilst Elster and Geitel ("Ann. der Physik," 2, 39, 321, 1890) and Well and Kopp ("Jahresber. Chem.," 270, 1889, 322, 1890) observed the formation of ozone by passing oxygen over hot platinum, indicating the reversibility of the catalytic activity of the platinum.

In many cases the activity of these catalytic materials

can be attributed to the formation and subsequent decomposition of an unstable oxide or peroxide, e.g.

$$2Ag + O_3 \rightarrow Ag_2O + O_2 \rightarrow Ag.$$

Manchot ("Ber.," **39**, 1510, 1906; **40**, 2801, 1907; and **42**, 3918, 1908), as a result of a series of experiments, obtained some interesting results with silver as a catalytic agent. He noted that pure silver was relatively stable in the presence of ozone, it being necessary to warm the metal up to 94° C. before decomposition of the ozone and formation of silver oxide occurred.

A trace of iron, usually obtained from the emery powder employed for cleaning the silver, serves as an excellent catalyst promoter, silver containing but a minute trace of iron reacts already at normal temperatures, and less than 0·01 per cent. of ozone can be detected by the reaction. Manchot states that silver thus prepared is even more sensitive than alcoholic tetramethyl base paper and that the ozone present in hot flames can easily be detected.

J. Strutt ("Proc. Roy. Soc.," **87**, 302, 1913) examined Chapman and Jones' results from a statistical point of view. He showed that in the case of catalytic decomposition at a gas-solid surface, the rate of decomposition depends on the number of collisions of a gas molecule with the surface necessary to effect the rupture of the molecule or reaction with the surface.

Calculating the number of collisions necessary to effect the decomposition of ozone in the presence of metallic silver from the minimum area of silver necessary to effect such change, he showed that only 1·6 collisions of an ozone molecule with the silver was necessary, or practically every col-

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lision was effective. In the absence of any surface, i.e. in free space, Strutt concluded that at 100° C. two molecules of ozone must collide 6×10^{11} times before a favourable collision resulted.

The effect of various gases on the rate of decomposition of ozone was likewise investigated by Chapman and Jones, who showed that oxygen, nitrogen and carbon dioxide had no effect, whilst nitrogen dioxide and chlorine accelerated the rate of decomposition. The influence of water vapour was not very marked. Shenstone ("Trans. Chem. Soc.," **71**, 47, 1897) stated that water vapour did not retard the formation of ozone; but, as pointed out by Armstrong, Shenstone probably included any nitrogen dioxide formed at the same time in his ozone estimations. Warburg and Leithauser ("Ann. der Physik," IV, **20**, 757, 1906) found that the formation of ozone was retarded by water vapour whilst the rate of decomposition was not affected. The specific influence of water vapour in accelerating the decomposition of ozone was, however, noted by Warburg ("Sitzungs K. Akad. Wiss.," Berlin, 644, 1913) in the course of his investigations on the photo-catalytic decomposition of ozone.

It may be concluded from these experiments, as well as from the somewhat scanty data collected on the rate of decomposition of ozone in solutions, that water vapour exerts a slight yet distinct catalytic action. This is only to be expected if it can be assumed that ozone is slightly acidic, since when passed into strong alkalis it forms the somewhat unstable coloured ozonates MHO_4. In this case (see Chapman and Jones, "Trans. Chem. Soc.," **208**, 1811, 1911) an equilibrium is probably set up represented by the equation—

$$2OH + 2O_3 = 2HO_4$$
$$2HO_4 = H_2O_2 + O_2 + O_3$$

If the rate of decomposition in the presence of moisture is thus accelerated by the HO_4 ion then the observed rate of decomposition will be

$$\frac{dc(O_3)}{dt} = K'(O_3) + K''(O_3)(OH),$$

where $C'(OH)$ is very small and K relatively small compared to K.

Roth ("Monatshefte," **34**, 665, 1913) investigated the decomposition of ozone in acid solutions, he showed that the rate of decomposition in strong acids was nearly bimolecular and in very weak acids practically unimolecular, the rate for any acid strength being determined by the equation

$$\frac{dc(O_3)}{dt} = K'(O_3) + K''(O_3)^2,$$

by suitable choice of the values from K and K, the velocity coefficients.

The catalytic activity of light in decomposing ozone was first studied by Regener ("Ann. der Physik," **32**, 1015, 1909), who showed that light of a certain wave length in the ultra violet portion of the spectrum, viz. in the region 240 to 300 $\mu\mu$, exerted a very marked deozonising action, and we have already discussed the interesting fact that light of shorter wave length exerts an ozonising action.

The reaction of kinetics of this reaction was investigated by von Bahr ("Ann. der Physik," **4**, 44, 598, 1910), and especially by Weigert ("Zeit. Phys. Chem.," **80**, 78, 1912), who showed that with complete absorption of light the reaction velocity of decomposition was proportional to the ozone con-

centrations. On the other hand, under conditions of homogeneous illumination, when the emergent and entrant beams are equally intense, conditions obtaining approximately in very thin gas films, the reaction velocity was found to be proportional to the square of the ozone concentration. From Weigert's data it may be calculated that in his experiments, approximately 100 molecules of ozone were decomposed per quantum of light energy absorbed. We have already noted that the magnitude of the quantum $h\nu$ necessary to effect any given photo-chemical action increases as the required energy increases, and consequently the photo-chemical activity of light is greatest as we approach the extreme ultra-violet. In the case of the formation of ozone from oxygen we have already discussed the effect of quanta of various magnitudes on both the oxygen atom and molecule; we would expect that the magnitude of the quantum necessary to detach an oxygen atom from an ozone molecule would be very small, on account of its instability; and again that the period of natural vibration of an ozone molecule, which determines the absorbtive power for light of a definite wave length, would be larger than that for the smaller oxygen molecule or atom. Both these expectations are fulfilled in the experimental results since deozonising light has a longer wave length than that effective in ozonisation. Photo-chemical equivalence, however, is not obtained as in the case of ozonisation. The absorption of a quantum of light energy by the already extremely unstable ozone molecule causes it to explode with considerable violence, and, as we have seen, the energy liberated during the explosion is able to cause the primary and secondary decomposition of over 100 other molecules before

the energy is dissipated into the surrounding medium. M. Saltmarsh ("Proc. Phys. Soc.," **27**, 337, 1915) regards the ultra-violet light in deozonisation as the source of energy in the ozonised oxygen which serves as centres of decomposition. Similar results were obtained by E. Warburg ("Berlin Akad. Sitzungsber.," **2**, 644, 1913). He obtained values for the specific photo-chemical activity by filling a little quartz cell with ozonised oxygen and exposing it to radiation for a definite length of time.

The specific photo-chemical activity ϕ was obtained from the ratio :

$$\phi \quad \frac{m}{E} \quad \frac{m_0}{}.$$

where E is the energy absorbed from the light, m_0 and m the ozone concentration before and after irradiation.

The rate of deozonisation was calculated from the relationship—

$$\frac{dc(O_3)}{dt} = \phi AJ \quad qm$$

J Light energy in gm. calories per second

A Fraction of light energy absorbed $\quad am$

m Concentration of ozone in cell.

q A cell constant correcting for the spontaneous decomposition of the ozone in the cell.

Hence $$\log \frac{m}{m_0} = t \log \phi AJ + q,$$

and in the absence of radiation :

$$\log \frac{m'}{m_0} \quad t \log q$$

He obtained the following values for the specific photo-chemical activity with light of wave length $\lambda = 253\ \mu\mu$ for

Ozone in	$\phi \times 10^5$.
Oxygen	0·253
Nitrogen	0·975
Helium	1·520

Hautefeuille and Chappuis ("C.R.," **91**, 762, 1880) were the first to notice the inhibiting effect of chlorine on the formation of ozone, which result was confirmed by Shenstone and Evans ("J.C.S.," **73**, 246, 1898). The work of Bodenstein and others on the hydrogen chlorine combination leads one to conclude that chlorine is an optical sensitiser for the decomposition of ozone. F. Weigert ("Zeit. Elektrochem.," **14**, 591, 1908) clearly showed that ozone containing small quantities of chlorine was rapidly decomposed by blue and violet light, whilst pure ozone is, as we have seen, only sensitive to ultra-violet radiation. The rate of decomposition was found to be proportional to the intensity of the light and independent of the ozone concentration. It would appear that the molecules of chlorine absorb the smaller quanta of longer wave length and are consequently endowed with an excess of kinetic energy equal in magnitude to the quantum absorbed. By subsequent collision with an ozone molecule this increment of energy is transferred, causing a rupture of the ozone molecule into oxygen. The chlorine molecule thus serves as a conveyor of energy and makes the medium sensitive to this particular radiation frequency.

CHAPTER IX.

INDUSTRIAL USES OF OZONE.

Applications to Hygienic Purposes.

The Sterilisation of Water by Ozone. The earliest experiments on the use of ozone as a germicide for the sterilisation of water were made by De Méritens in France (1886).

He showed that even dilute ozonised air would effect the sterilisation of polluted water, provided that intimate contact between gas and liquid was effected. A few years later the subject was reinvestigated by Fröhlich ("Elektrochem. Zeit.," 344, 1894), of the firm of Siemens and Halske, who erected a semi-technical experimental plant at Martinikenfeld. Ohmüller and Prall ("Arbeit. Kais. Gesund.," 229, 1902), at the request of the German Government, investigated the process in great detail and as a result showed that ozone energetically attacked bacteria in water from which any excess of inert organic matter had been previously removed. Sufficient evidence as to its practical utility was thus at hand to warrant a closer examination as to its suitability for municipal work.

Chemically, ozone is the ideal agent for purification, since it leaves behind it nothing foreign in the treated water, with the exception of oxygen, which assists in the normal aeration and greatly augments the palatability of the water.

For technical purposes, however, the important factors of reliability and cost are all important.

As a result of Fröhlich's experiments and the satisfactory report of Ohmüller and Prall, the firm of Siemens and Halske developed their process of sterilisation with ozone, and large plants were installed at Wiesbaden and Paderborn and at a later date at St. Maur, Paris, and Petrograd.

Contemporary with these developments, Tindal, Schneller and Van Sleen installed an ozone sterilisation plant at Oudshoorn in Holland which was subjected to a detailed investigation by Van Ermengem on behalf of the Belgian Board of Agriculture, and by Drs. Ogier, Roux and Repin ("Rev. Gen. des Sciences," 596, 1896) for the municipality of Paris, with the result that an ozone installation on Tindal and de Frise's system was installed at St. Maur, Paris. At a later date a combination of the Tindal-de Frise and Siemens-Halske systems was utilised by the Parisian municipal authorities.

In 1898, Abraham and Marmier erected an installation at Lille, and in 1904 an ozone plant on Otto's system was supplied to the municipality of Nice.

Small installations were likewise erected on Vosmaer's system in Holland and at Philadelphia, U.S.A.

As a result of these developments at the present time there are in operation over fifty plants for the industrial sterilisation of water by this means.

We have already given a brief description of the various types of ozonisers developed for the purpose of the economical production of ozonised air; the various installations naturally differed in their methods of ensuring contact of the water

with the ozonised air and in the preliminary treatment of the water.

Systems of Ensuring Intimate Contact Between the Ozone and Water.—In the earlier Siemens and Halske installations at Wiesbaden and Paderborn, ozonised air containing from 2½ to 3 grammes of ozone per cubic metre passed upwards

FIG. 31.

through a tower filled with broken flint and met a descending current of water which had passed through roughing filters.

Fairly satisfactory bacterial reduction was effected by this method, the count ranging from 9 to 2 organisms per c.c. after ozonisation, and these organisms were of the resistant and harmless B. subtilis types. Economically,

however, these contact towers left much to be desired, the cost being about 2·75d. per 1000 gallons of water treated.

The fundamental point to be considered in the design of a contact tower, viz. the intimate contact of every drop of water with the ozonised air, was clearly not realised in this elementary type of tower. It is evident that every flint is covered with a thin film of water into which the ozone can only penetrate by diffusion. Now the rate of diffusion of the ozone into the liquid film is proportional to its partial pressure in the gas above the film and approximately inversely proportional to the square root of its density. Thus, although it is not a difficult matter to oxygenate water in this type of tower by means of air, since the partial pressure of oxygen in air is about 20 per cent. of one atmosphere, yet in the case of ozonised air containing 2·4 gms. per cubic metre the partial pressure of ozone is only 1/1000 of an atmosphere and its relative rate of diffusion only $\sqrt{\frac{32}{48}}$, or three-quarters that of oxygen. As a consequence, to ensure sterility, high concentrations of ozone had to be employed and much ozone was lost at the top of the tower.

Trouble was also caused, especially at Wiesbaden, by clogging of the contact tower with precipitated ferric hydroxide. The water contained small quantities of ferrous salts up to 0·5 parts per million, which were precipitated on oxidation as ferric hydroxide in the interstices of the quartz packing.

Vosmaer states that by proper design of this type of tower, relatively long and slender in proportion, sterilisation can be accomplished by using an ozone concentration of only 1 gramme per cubic metre, and that complete removal

of the ozone is effected by such a tower when gas and liquid flow rates are properly adjusted; thus a tower 1 foot in diameter and 33 feet high was shown capable of treating 10,000 gallons an hour, one 3 feet diameter at Philadelphia dealt with 50,000 gallons per hour.

In the first plants of Tindal and de Frise both ozonised air and raw water entered by separate pipes at the base and flowed in the same direction through the flint packed tower, which was divided up into segments by means of perforated metal or celluloid plates.

FIG. 28

A considerable advance on this practice was made by Otto by the introduction of an emulsifier for ensuring intimate mixture of ozonised air and water at the base of the tower. The emulsifier is constructed on the lines of a Korting injector or simple water vacuum pump, the water supplied under pressure drawing in the ozonised air under vacuum. Not only was a very intimate mixture of the ozone and the water effected by this means but by utilising the vacuum produced by the water stream the necessity for pumping ozonised air, which requires pumps of special construction is avoided. Otto's installation at Nice included a sectional contact tower of cement using shingle as packing, and

operated by means of these emulsifiers. The plant is capable of dealing with 5,000,000 gallons per day.

In the Otonair System, which has been successfully developed for installations of capacity from 1000 to 2000 gallons per hour, the ozonised air is drawn into an injector by the pressure of the water which is of the order of about two atmospheres. It is thoroughly emulsified by the injector and passes into a sterilising tank which is so proportioned as to give a contact of about 80 minutes. The concentration of ozone used is from 2 to 3 gms. per cubic metre produced in the standard type of ozonisers (see p. 129).

The greatest economy in the utilisation of ozone was effected by de Frise, who introduced a cyclic system at the St. Maur waterworks, where it operated with great success.

A diagrammatic sketch of De Frise's system is shown below.

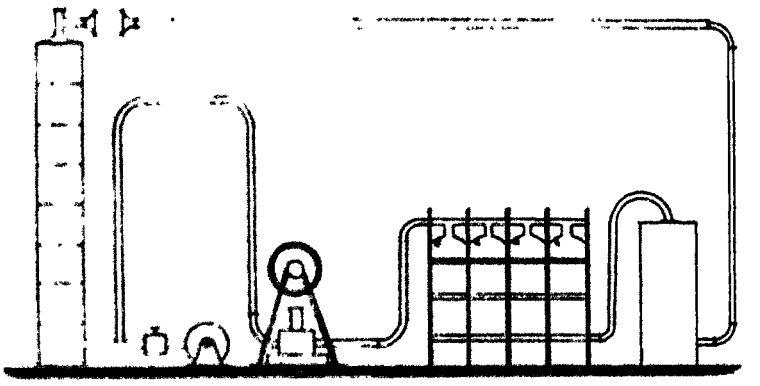

FIG. 23.

The ozone compressor draws the ozonised air from the ozonisers and forces it into the plate sterilising tower; from the top of the steriliser the air returns to the ozonisers,

passing on its way through a separator and a dryer in which it comes in contact with calcium chloride, which is cooled in hot weather. A small suction valve on the inlet of the separator admits fresh air to make up for the loss through absorption by the sterilised water. The sterilising tower is constructed on the sectional system, being built up of enamelled iron sections 20 inches deep and 3 feet in diameter, each section (there being 30 sections in the tower) being separated from the others by perforated plate.

With a ratio of ozonised air to water of two to five, 88 per cent. removal of the ozone is effected in the tower system, the residue being returned after drying to the ozonisers.

Pre-treatment of the Water. Since inert organic matter is readily oxidised by ozone to carbon dioxide and water, in order to exercise every possible economy in the utilisation of ozone, it is necessary to subject polluted waters to some form of preliminary purification.

The earlier installations at Wiesbaden and Paderborn were equipped with simple roughing filters with small pebbles as filtration medium, through which the water passed at relatively high speeds. In the later plants, where it was realised that the cost of removing organic matter by oxidation with ozone was higher than by the usual methods of sedimentation and filtration, more attention was paid to the pre-treatment of the water, and the ozone was utilised merely to remove the last traces of organic matter and ensure sterilising of the water, conditions unobtainable by any method of sedimentation and filtration except at prohibitive costs.

In the Otto installation at Nice sand filtration alone is

employed as pre-treatment. At Ginneken, in Holland, the Mark water is subjected to gravel filtration, followed by a sand filter. At Oudshoorn the Rhine water is passed through sedimentation basins and sand filters prior to sterilisation. At St. Maur, Paris, sedimentation basins in conjunction with gravel and sand filters are utilised for the Marne water, whilst at Petrograd the Neva water, which is subjected to very serious pollution and liable to contain pathogenic organisms, is passed through a battery of mechanical filters using alumina as coagulant prior to the ozone treatment.

For the sterilisation of upland waters which are subjected to sporadic or occasional pollution such pre-treatment is generally unnecessary, especially in those cases where adequate storage is provided by means of impounding reservoirs which act as sedimentation basins of large capacity. Exceptions, however, are to be found when the upland water is derived from a peaty or recently flooded watershed, where, during the summer months, the quantity of oxidisable organic matter in the water suffers a considerable augmentation and necessitates a correspondingly increased dosage of ozone.

For the treatment of river supplies which are already polluted, and with the growth of the riparian population are becoming increasingly contaminated in organic matter, some form of pre-treatment is necessary, and it must be emphasised that the utility of ozone in the present stages of its industrial manufacture is most marked when it is employed as a finisher or sterilising agent for waters which are already good enough but not safe enough for public supplies, rather than when attempts are made to purify highly contaminated streams.

Results Effected by Ozone Treatment

The change in appearance of many waters after ozonisation is frequently very striking, and leads to the removal of traces of coloured organic compounds and to the aeration and oxygenation effected during the process. Many river polluted river waters, which after chemical treatment and sand filtration, are brown or pale yellow in colour, and generally flat and insipid, after ozonisation become bright and sparkling, generally with a slight opalescent and bluish tint.

The physical changes are accompanied by chemical changes no less marked and characteristic of the process, thus the oxygen consumed figure determined by the permanganate under standard conditions (4 hours at 80° C. in acid solution, is usually reduced from about 60 per cent., as is indicated by the following figures:

Installation.	Oxygen Consumed Figure (Part per 100,000)		Percentage
	Before Treatment	After Treatment	
Nice	1·4	0·6	[illegible]
Somme	0·11	0·1	Nearly [illegible]
St. Maur	0·121	0·044	36·3
Philadelphia		Reported as satisfactory	Satisfactory

The quantity of organic matter oxidised by the ozone as indicated by the difference in the oxygen consumed figures naturally varies with the three factors, the nature of the organic matter, the concentration of the ozone, and the time

of contact between the ozone and the water. Thus S. Rideal ("J. Roy. S. Inst.," 30, 32, 1909) found at St. Maur the following distribution of the ozone at two different gas concentrations: –

Ozone in Gms. Per Cubic Metre, in		
Entering air	1·68	2·65
Entering water	0·679	1·071
Escaping into the air	0·137	0·291
Escaping in solution in the water	0·048	0·162
Used in oxidising organic matter	0·494	0·618
	Gms. Per Cub. Metre.	
Oxygen consumed for the water untreated (from acid $KMnO_4$ at 80° C.)	1·73	1·12
Oxygen consumed for the water treated (from acid $KMnO_4$ at 80° C.)	1·25	0·61
Decrease	0·48	0·51
	= 28 %	= 45 %

During these experiments it was noticed that the dissolved ozone left in the water after it left the ozonising column disappeared after a few hours, and it seemed probable that oxidation of the more resistant organic matter was still proceeding. This was confirmed by the determination of the oxygen consumed figures from time to time.

Two typical tests giving the following results :—

	Oxygen Consumed Gms. Per Cubic Metre.	
Filtered water	1·73	1·12
After ozonisation	1·25	0·61
One hour later	1·15	0·58
Two hours later	0·90	0·51

A corresponding decrease in the free and albuminoid ammonia takes place simultaneously with the reduction in

the oxygen consumed figures, as is shown from the investigations of Van der Sleen on the Seine water:

	Before ozonisation	After
Free ammonia	0·51	0·1
Albuminoid ammonia . .	0·16	0·1

As in the case of the organic matter in the water, a marked reduction in the number of bacteria takes place. In common with other germicides ozone possesses elective action on micro-organisms, certain organisms being more resistant than others to its action. It so happens that pathogenic organisms which are already enfeebled by their unsuitable environment are easily destroyed, whilst the non-pathogenic sporing organisms, such as B. subtilis, are frequently found in ozonised waters. This point was fully investigated by Otto in his experiments on the treatment of the Seine and Vanne waters.

He showed that all pathogenic organisms and the following common bacteria which he isolated were rapidly removed: these included B. fluorescens liquefaciens, B. coli, B. typhosus, B. proteus vulgaris, B. prodigiosus and Aspergillus niger. More resistant were B. subtilis, B. luteus and Penicillium glaucum, which only succumbed to prolonged treatment with ozone.

Camlette showed that Lille installation effected an average reduction in the bacterial pollution of the water from 28180 per c.c. in the untreated water to 10 c.c. in the treated water; these latter were found to consist entirely of the B. subtilis type. These conclusions were confirmed by S. Rideal in his investigations on the Siemens-de Frise plant at St. Maur. In the filtered water, prior to ozonisation, B. coli was usually

present in 40 c.c. of water and occasionally in 20 c.c., whilst it was never found in the treated water. The 20 c.c. count was reduced from an average of 74 to 1·1 per c.c., which were found to be spore-bearing organisms of B. subtilis type. Whilst purification can be effected by the consumption of 0·5 gms. of ozone per cubic metre of water, the ozone consumption per cubic metre of water naturally varies with the quality of the water to be treated, the economic limit appears to be in the neighbourhood of 2 gms. ozone per cubic metre of water. If, by preliminary testing with permanganate, it is found that more than this quantity would be required then some form of preliminary treatment is essential for economic operation.

The Purification of Air.

Several types of apparatus have been designed for the the purification of air in confined spaces, such as theatres, lecture halls, slaughter houses, tanneries and breweries, whilst extended use of ozonised air has been made upon the Central London Railway systems and public lavatories.

Although the immunity of the motor drivers on the London Tubes during the recent epidemics of influenza has been somewhat remarkable it is more probable that this must be attributed to the uniformity of temperature and to the circulation of the air rather than to any specific action of the ozone in the air.

The evidence for the specific utility of ozone as a means of purifying air is somewhat conflicting.

Dewar and McKendrick ("Pogg. Ann.," **152**, 329, 1874) showed that by the inhalation of strongly ozonised air the frequency of pulsation of the heart is lowered very consider-

ably, the blood temperature sinks from 3° to 5°, and post mortem examination showed that the blood had become venous in appearance. Thenard ("C. R.," **82**, 157, 1876) and Biny ("Med. C. Bl.," **20**, 721, 1882) confirmed the observations of Dewar's. Schultz ("Arch. f. Exper. Path. u. Pharm.," **29**, 365, 1892) records several cases of chronic poisoning by ozone. Jordan and Carlson[1] ("J. Amer. Med. Assoc.," **61**, 1007, 1913) confirmed the deodorant action of ozone on air but showed that long before the concentrations reached those necessary for germicidal action injury was caused to the respiratory tract.

The lowest concentrations of ozone in air which can exert a definite disinfecting action (Schultz, "Zeit. f. Hyg.," 75, 1890; and de Christmas, "Ann. de l'Inst. Pasteur," **7**, 690, 1893) appears to be in the neighbourhood of 1·333 mgm. per litre. With such concentrations sterilisation can usually be effected in air, but the presence of large quantities of moisture lowers its germicidal activity. According to Labbé and Ondin ("C.R.," **113**, 111, 1891) the highest concentration which may be inhaled without deleterious effect is approximately 0·11 to 0·12 mgm. per litre.

They state that beneficial results obtain by the inhalation of ozonised air of this concentration, a marked increase in the oxyhæmoglobin content of the blood taking place after an interval of from ten to fifteen minutes.

It is therefore evident that there is no question of germicidal activity in ozonised air of concentrations suitable for respiration. As a powerful oxidant it doubtless removes

[1] Leonard Hill and Flack ("Proc. Roy. Soc.," **B 84**, 404, 1911) state that a concentration of 1 in 100 of ozone produces irritation of the respiratory tract.

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small traces of hydrogen sulphide and other impurities in air, whilst the unpleasant smells associated with crowded places are amenable to treatment with oxidising agents such as ozone. It is somewhat remarkable that most odoriferous substances contain unsaturated valencies and as such would naturally be attacked by means of ozone. The odour of ozone in itself when very dilute is by no means unpleasant and thus provides a counter irritant to the olfactory organs, a matter of psychological importance if of no physiological significance.

The use of ozone even in dilutions of 0·11 to 0·12 mgm. per litre has frequently been condemned on account of its supposed physiological activity, in many cases erroneously, since, unless the usual precautions such as drying the air and the avoidance of sparking are taken in the preparation of the ozonised air, oxides of nitrogen are liable to be formed which have an extremely high physiological activity even in extreme dilutions. Schwarz and Muenchmeyer ("Zeit. f. Infekt. Krankh." **75**, 81, 1914) investigated in great detail the deodorising action of small concentrations of ozone in air; they observed that hydrogen sulphide was rapidly oxidised, sulphur dioxide slowly converted to sulphuric anhydride, whilst the mercaptans, skatol, and indol were oxidised to somewhat pleasant smelling substances.

Carbon monoxide was but slowly oxidised whilst ammonia was not affected. Franklin ("IV. Int. Congress on School Hygiene," 1913) and Rosenfeld and Egidius ("Zeit. Anorg. Chem.," **85**, 217, 1914) confirmed these observers' results on the action of ozone on hydrogen sulphide. This reaction was studied in detail by Rosenfeld, and it was found that oxidation takes place through a series of intermediate compounds according to the following scheme:—

Sulphide → thiosulphate $\left\{\begin{array}{l}\text{hyposulphate, sulphite}\\ \text{polythionate}\end{array}\right.$ → dithionate → sulphate.

Although the germicidal activity of ozone in concentrations which exert no injurious action on the tissues of animals is practically negligible, yet it has been found by Hyde that sterilisation is effected by ozonation of air, and much reduction is obtained in the bacterial contents of the air which has actually passed through the ozonizer. The air, which has been relatively strongly ozonised and subjected to the ultra-violet radiation in the ozonizer, is practically sterile, and a consequent improvement in the bacterial pollution of air which has been admixed with the purer air was naturally expected and in fact obtained. The largest system of air purification by means of ozone is that of the Central London Railway which is equipped with air screens, washers, and ozonizers of the Ozonair type. The total air supply treated for this system being of the order of eighty million cubic feet per day. The average concentration of ozone in the Tube air is of the order of one part in two millions (1·2 mgm. per cubic metre) which, under special circumstances, it is stated that it is increased to five parts per million (6·2 mgm. per cubic metre).

The installation on the Central London Railway was so successful in operation that the system of ventilation has been extended to practically every other London Tube.

Surgical and Therapeutic Uses of Ozone.

During the period of the war small portable ozonizers have been in use in many of the military hospitals of the nations for the treatment of wounds. Major Stokes, of the

Queen Alexandra Military Hospital ("Lancet," 1918), describes the following method of wound sterilisation which appears to have given excellent results. Wounds and sinuses are washed twice daily with boiled water and a dressing of oxy gauze is applied. The ozone (ozonised air) is applied on the wounded surface or on to the cavities and sinuses twice daily for a maximum time of fifteen minutes or until the surface becomes glazed. At first ozone causes an increase of the discharge of pus, which is gradually replaced by clear serum. The serum at a still later stage becomes coloured reddish or purplish. It was found that ozonised air applied in this way was a strong stimulant, and increased the flow of blood to the affected part, that it was a germicide and exerted great powers in the formation of oxyhæmoglobin. A record of seventy-nine cases so treated is given, in which the period of treatment varied from a few days to three months and was in practically all cases completely successful.

Curle ("Practitioner," 864, 1912) describes the application of ozonised air to the liberation of iodine in the lungs for the treatment of phthisis. Potassium iodide is introduced into the lungs by ionisation, and the iodine is subsequently liberated by the inhalation of ozonised air. For disinfection of the intestinal canal in cases of enteritis and dysenteries, Lessing ("Lancet," Nov., 1913) records the improvement obtained by washing out the intestinal canal with ozonised water. The treatment of ulcers and pyorrhœa of the teeth has been successfully accomplished with ozonised air. Ozonised medicaments and ointments, such as vaseline, have been stated to possess a superior curative value to those not so treated. Ozone appears to be slightly soluble in these semi-fluid

hydrocarbons, and would naturally give the same treatment a germicidal activity. Information is not available as to the extent of the solubility of ozone in water for this purpose, or how long the substance retains any germicidal activity due to dissolved ozone or to the presence of ozonised air.

As has already been mentioned the passage of ozonised air in timulating the production of chlorophyll has been successfully utilised for the treatment of certain forms of anæmia, whilst its application in cases where there is a deficiency of oxygen absorbed in the system, such as in asthma or heart weakness, is not without benefit.

Applications for Bleaching Purposes

Houzeau ("C. R.," 75, 1699, 1872, and "Bull. Soc. Chim.," 30, 1187, 1878) showed that dilute ozonised air possessed in common with chlorine and bromine the property of selectively oxidising the colouring matters present in various natural substances. Ozone appears to be even more effective than either chlorine or bromine, since not only is the danger of forming coloured substitution chloro- or bromo-derivatives avoided, but the oxidising power of ozone greatly exceeds that of chlorine or bromine. For this reason only very dilute concentrations of ozone may be utilised for bleaching purposes, and many unsuccessful results are directly attributable to the employment of air relatively highly ozonised.

Fibres

Linen and cotton goods are slowly attacked by ozone ("Bull. Soc. Ind. Mulhouse," 38, 91, 1868), and according to Witz ("Bull. Soc. Rouen," 11, 198, 1883), in the presence of moisture, oxycellulose is formed. The subject

was reinvestigated by Cunningham and Dorée ("J.C.S.," 103, 1347, 1912) employing high concentrations of ozonised oxygen (20 to 25 gms. per cubic metre). They showed that an oxycellulose and cellulose peroxide accompanied by a destruction of the fibre were produced with the liberation of carbon dioxide.

Unbleached samples of cotton became white in from one to two hours, but when dried the fibre was found tendered and dusty. Jute fibres were likewise rapidly bleached, but became acid and tender when subjected to a similar treatment for a few hours. The cellulose peroxide affected a photographic plate, and possessed oxidising properties such as the liberation of iodine from potassium iodide. In the presence of water hydrogen peroxide was formed. In general the action of ozone on cellulose closely resembles that of ammonium persulphate ("Ditz Chem. Zeit," 31, 833, 1907; "J. Prakt. Chem.," 78, 343, 1908), and with more dilute concentrations of ozonised air bleaching without subsequent tendering might be obtained.

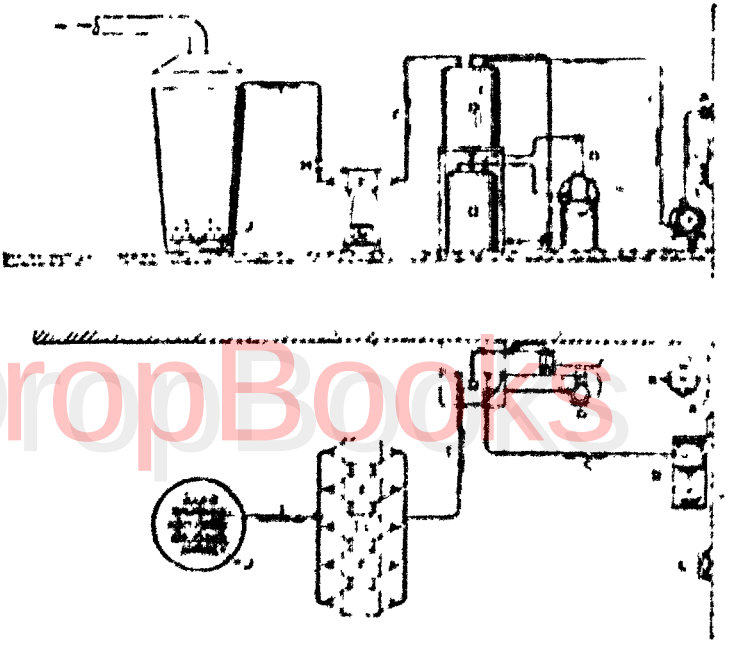
The application of ozonised air to the conditioning of textile materials is stated to be entirely successful; exceedingly dilute concentrations of ozonised air are employed, and under suitable conditions of humidity the period of conditioning can be reduced from several months to a few days.

Oils, Fats, and Waxes.

The applications of the use of ozone in the oil, fat, and wax industries are very considerable, the reagent being useful for a great diversity of purposes. Amongst the more important of these may be mentioned:—

1. Removal of odour, flavour, and colour from oils and fats intended for edible purposes.

2. Bleaching and refining of oil and fat for use in the soap industry.



A Air Cleaner
B Electrically driven Blower
C Air Delivery Pipe
D Air Cooling Machine
K Electric Motor
E Cold Air Delivery Pipe
F Ozone Generators
G Transformer
H Valve
I Ozone Pipe
J Ozone Injectors
L Switchboard

FIG 21.

3. Bleaching of oils for paint and varnish-making.

4. Bleaching and refining of waxes for use in the manufacture of candles, polishes, and ointments.

In the above sketch is given a diagrammatic arrange-

ment of a bleaching plant on the Ozonair system. The temperatures at which selective oxidation of the colouring matter or objectionable odoriferous substances in the oil, fat, or wax commences, the concentration of ozone, and the period of action naturally vary with the nature of the substance treated and the degree of refining required. Generally a fairly dilute concentration of ozone at not too elevated temperatures passed through the material for a relatively long time gives the best results. In certain cases it is found advantageous to add small quantities of catalytic materials, such as salts of manganese, vanadium, or cerium, to accelerate the process of oxidation.

The application of ozonised air to the bleaching and deodorisation of oils, fats, and waxes is well exemplified by the following list (see pp. 162, 163), in which a summary is given of the effect of dilute ozonised air on various commercial products.

Application to the Paint and Varnish Industry.

As has already been observed all the industrial oils and waxes readily undergo partial or complete deodorisation by fractional oxidation of the coloured chlorophyllic constituents utilising ozonised air as oxidising agent. For the production of clear and transparent varnishes this is a matter of some technical importance, and the use of ozone for this purpose has been frequently suggested.

It would appear that the use of ozonised air as a substitute for siccatives in the preparation of drying oils is already out of the experimental state. It has long been known that the drying of oils is a process of slow oxidation and polymerisation (see Lippert, "Zeit. Angew. Chem.," 11, 412, 1895;

Oil, Fat, or Wax	Bleaches	Deodorises	Remarks
Arachis or ground nut	Yes	Yes	[illegible]
Bone fat	Yes	Yes	[illegible]
Horse Tallow	Yes		[illegible]
Cocoanut	Yes	Yes	[illegible]
Cocoanut oil	Yes	Yes	[illegible]
Cod oil	Yes	Yes	
Cotton seed	Yes	Yes	[illegible]
Japan wax tallow	Yes	Yes	Bleaches well and ships in good condition.
Lard oil	Yes	No	Bleaches very easily
Mowrah	Yes		Bleaches readily, but requires subsequent treatment for deodorisation and improvement of flavour
Neatsfoot oil	Yes	Yes	Bleaches readily
Oleine	Yes	Yes	Bleaches easily. At the same time the odour is much improved, but the characteristic odour still remains
Olive	Yes	Yes	Bleaches very easily, the darkest varieties, such as that known as "sulphur," are bleached to the ordinary olive colour.
Palm	Yes	No	Bleaches very easily in most cases. Even "unbleachable" varieties such as Congo and saltpond are much improved in colour
Sesame	Yes	No	Bleaches fairly easily according to grade or quality but requires subsequent treatment for deodorisation and improvement of flavour.

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[illegible]	Bleaches	Deodorises	Remarks.
Soya	Yes	Yes	Bleaches easily. At the same time the odour is much improved, but the characteristic odour still remains.
Stearate	Yes	Yes	Bleaches easily. At the same time the odour is much improved, but the characteristic odour still remains.
[illegible]	Yes	Yes	Bleaches easily. Odour is much improved.
[illegible]	Yes	Yes	Bleaches fairly easily according to grade or quality, but requires subsequent treatment for deodorisation and improvement of flavour.
[illegible]	Yes		There are at least twenty well-known commercial varieties all of which possess different characteristics, and respond to the treatment in varying degree. Some are bleached entirely by ozone, others only partially, so requiring subsequent sun treatment in the ordinary way. Contrary to what might be presumed, the dark varieties, such as "Cuba" or "West Indian," give the best, whereas the lighter varieties may give the least satisfactory results.
Carnauba	Yes		—
Carnauba	Yes		—
[illegible]	Yes		The bleaching is effected very readily after removal of all the free fatty acids. The degree of colour or bleach obtained depends very much on the quality of the original wax and the care with which it has been collected.
Montana	Yes		

[illegible] In all these cases, if deodorisation only is desired, this can be obtained in many cases by using a low concentration of ozone and without any subsequent treatment, but when bleaching and deodorisation are both required, subsequent treatment will be necessary.

[illegible] It has been stated that the actual cost of bleaching and deodorising oils and fats for edible purposes or for soap making, by means of ozonised air, does not exceed five shillings per ton, a figure which compares quite favourably with the alternative methods of treatment with superheated steam, fuller's earth or bone filtration.

Weger, "Chem. Rev. Fett Harz Ind.," 4, 301, 1899). A Genthe ("Zeit. Angew. Chem.," 19, 2057, 1906), who investigated the process in detail, showed that the action was autocatalytic in character, or that the rate of oxidation of the oil after a time when a quantity x had already been oxidised was given by the equation $\frac{dx}{dt} = K(a - x)(b + x)$, where a and b were the initial concentrations of linseed oil and catalyst originally present. Further experiments (see also Engler and Weissberg, "Chem. Zeit.," 27, 1136, 1903) showed that the catalytic material naturally formed was some form of unstable peroxide which accelerated the oxidation of the oil by air.

This unstable peroxide could be supplemented or replaced by other peroxides of a similar character, such as those obtained on the exposure of turpentine to the air or even by the agitation of an ether air mixture. These peroxides are destroyed by boiling the oil but can be regenerated by aeration. (For a consideration of the composition of these peroxides formed in the drying of linseed oil see Orloff ("J. Russ. Phys. Chem. Soc.," 42, 658, 1910), Fahrion ("Zeit. Angew. Chem.," 23, 723, 1910), Salway and Kipping ("J.C.S.," 95, 166, 1909), and others.)

The addition of siccatives, such as salts of lead, manganese zinc, frequently with the addition of certain promotors as cobalt, vanadium, cerium, and uranium is now common practice. The salts are either those of weak acids such as the borates, or of soluble organic acids and oleates, linoleates, or resinates (see Ingle, "J.C.S. Ind.," 454, 1917). The siccatives are pseudo-catalytic in behaviour, and serve to

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stabilise or assist in the formation of the auto-catalytic peroxide.

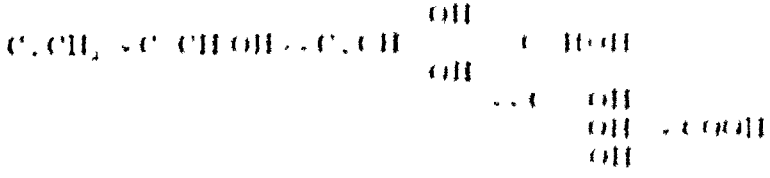
Identical results are obtained with the use of ozonised air, the oils can be easily thickened and the process conducted at much lower temperatures. Linseed, chinese wood, poppy seed, rape, and similar oils, rapidly thicken at comparatively low temperatures (upwards of 35° C.), and at the same time their colour is much improved by selective oxidation of the coloured constituents. Bleaching usually proceeds anterior to the thickening process, consequently an improvment in colour may be obtained without drying the oil.

Linseed oil may readily be thickened to a syrup or to a jelly for the manufacture of linoleum; Chinese wood oil likewise rapidly undergoes oxidation, whilst poppy-seed and rape oils thicken less readily than linseed oil. The utilisation of ozonised air in the oxidation of linseed oils has naturally been extended from the simple preparation of drying oil to the drying of the oil in its various technical applications, such as linoleum manufacture, the preparation of waterproof materials, fish netting, and other similar manufactures.

Ozone in the Fine Chemical Industries.

The oxidation of organic substances by means of ozone has been the subject of numerous investigators. Carbon monoxide is readily oxidised to carbon dioxide in the presence of moisture (Clausman, "C.R.," 130, 1332, 1910), but only slowly when the gases are dry (Bemsen, "Ber.," 8, 1414, 1875). Aldehydes are readily oxidised to alcohols; iodobenzene to iodoso benzene whilst the saturated hydrocarbons themselves are readily attacked at low temperatures. Thus, methane is

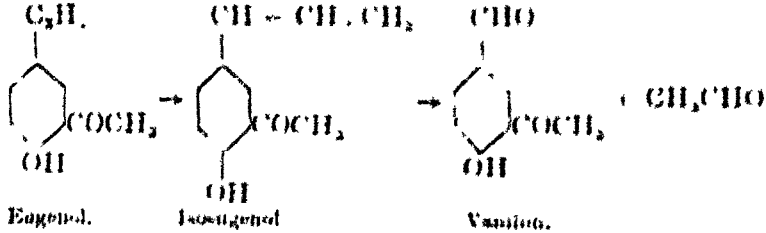
converted below 100° (Fenton and Gostling, *Trans.*, 89, 1911, 1906) has shown that reduction of the oxygen atom takes place, the corresponding alcohol is formed which is then oxidised rapidly to the more stable aldehyde and subsequently lower oxidation to the acid proceeds



Harries ("Ann.," **374**, 288, 1910) suggests that oxidation proceeds through the intermediate formation of unstable peroxides, e.g. $C_6H_5CH(OH)\cdot O\cdot O\cdot CH(OH)C_6H_5$, through a series of unstable hydroxyl atoms postulated by Dupuis.

Ozone is finding many applications as an oxidising agent in the fine chemical industries. It has been successfully employed for the preparation of several synthetic perfumes, such as the methyl ether of protocatechualdehyde (vanillin, piperonal (heliotropin), and musk aldehyde, the manufacture of vanillin being accomplished on a very large scale in France, America, and in this country.

Vanillin is prepared from eugenol according to the following scheme:



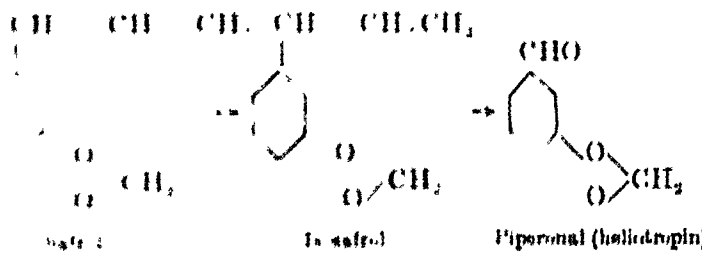
Eugenol. Isoeugenol Vanillin.

the isoeugenol being oxidised by ozone to vanillin and acetaldehyde by rupture of the double bond.

According to Trillat the process is conducted as follows: Eugenol is converted into isoeugenol by treatment with caustic potash and amyl alcohol, from which solution it is liberated by sulphuric acid.

About 25 litres of isoeugenol are dissolved in acetic acid and subjected to a current of ozonised air (2 to 2·5 gms. per cubic metre) for a period of six hours at a low temperature (ca. 2° C.) in an enamel-lined vessel fitted with a tall rectification column. When the oxidation to the aldehyde is completed the acetic acid is removed by distillation, ether and sodium bisulphate are added and the solution warmed to 30° C. The bisulphate aldehyde compound is washed with ether decomposed with sulphuric acid, and the vanillin finally extracted with ether.

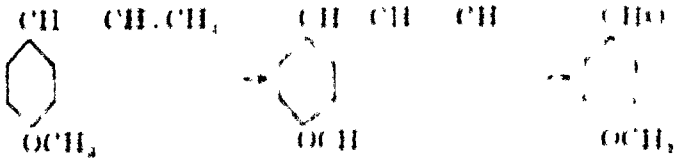
In a similar manner heliotropin is prepared from safrol according to the equations:



Safrol. Isosafrol. Piperonal (heliotropin).

The safrol is converted into isosafrol by heating with an alcoholic solution of caustic potash, from which it is subsequently extracted by means of ether. For treatment with ozone (as in the case of isoeugenol) it is dissolved in acetic acid, from which the heliotropin is recovered in like manner.

Anisaldehyde can be prepared in a similar manner by the oxidation of anethol

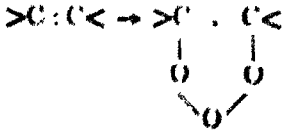


Attempts have also been made to utilise ozone for the oxidation of aniline to aniline black and the bleaching of various dyes, such as indigo, to the coloured dye stuffs, but do not appear to have received any extensive technical application.

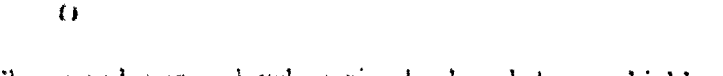
For analytical purposes in organic chemistry ozone merits some attention, since by the preparation of ozonides and their subsequent decomposition the structure of various complex compounds containing ethylene linkages has been elucidated.

The investigations of Harries (Ber., 37, 839, 842, 2708, 3431, 1904, *et seq.*) and his co-workers, have been the most remarkable in this direction. Unsaturated compounds are ruptured at the double bond and converted into aldehydes and ketones.

In the absence of water, however, a direct addition of ozone to the double bond occurs with the formation of ozonides—



which on the subsequent addition of water undergo decomposition to ketones and hydrogen peroxide—



The ozonides are colourless, viscid, oily substances, highly explosive and possessing a penetrating odour.

In common with ozone they affect a photographic plate, attributable to the chemoluminescence produced on oxidation of organic matter by means of ozone (see pp. 8, 159).

The ozonides behave like powerful oxidising agents themselves, akin to the peroxides in chemical behaviour in that they bleach indigo, liberate chlorine from potassium iodide and react with potassium permanganate.

Benzene trozonide or ozobenzene, isolated by Renard, is a relatively stable substance, easily produced by passing ozonised air into dry benzene, from which it is precipitated as a colourless amorphous product. It explodes somewhat violently on the addition of warm water.

Oleic acid, either when dissolved in acetic acid (Harries and Thieme, "Ber.," 30, 28, 11, 1905), or when treated with ozonised air without a solvent (Molinari and Soncini, "Ber.," 30, 27, 31, 1906), forms a normal ozonide. In chloroform four atoms of oxygen are taken up to form an ozonide peroxide.

By analysis of the products of decomposition the position of the unsaturated linkage in oleic acid was established between the atoms C_9 and C_{10}, thus giving oleic acid the structure $CH_3(CH_2).CH = CH(CH_2)_7.COOH$.

If strong concentrations of ozone be employed for the preparation of ozonides, oxozonides are said to be formed at

the same time (Harries, "Ber.," 43, 2356, 1910; see p. 181). Thus s. butylene yields the following oxozonides:—

(1) $CH_3.CH.CH.CH_3$ (2) $\begin{vmatrix} CH_3.CH.CH.CH_3 \\ O_4 \end{vmatrix}$

O_2

Normal oxozonide. Isomeric

(3) $CH.CH.CH.CH_3$

and

O_4

Oxozonide.

and a dimeric oxozonide:—

(4) $\begin{vmatrix} CH_3.CH.CH.CH_3 \\ O_4 \end{vmatrix}_2$.

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cyclopentene exhibits a similar behaviour in that the normal oxozonide and two oxozonides are formed on oxidation (Harries, "Ann.," 4, 4101, 1915).

Harries (*loc. cit.*) attributed the formation of oxozonides to the presence of oxozone in the ozonised oxygen which he postulated to be present by analysis, employing the iodide method of estimation. The existence of oxozone in ozonised air or oxygen has, however, not been confirmed (see p. 181) and some other structural formula must, consequently, be adopted for the oxozonides.

The ozonisation of rubber was first attempted unsuccessfully by Wright in 1897 ("Bull. Soc. Chim.," 18, 148, 1897), and was subsequently investigated in great detail by Harries and his co-workers, Langheld and Haeffner, in the hope of elucidating the complex structure of the isoprene polymer.

Harries ("Ber.," 37, 2708, 1904) ozonises rubber by the following procedure: Ozonised air, washed with caustic soda

and sulphuric acid to remove the oxozone, containing from 6 to 12 per cent. of ozone, is passed for ten hours into a 1 per cent. solution of purified rubber in chloroform. The end of the reaction is ascertained by the decolorisation of bromine.

The ozonide is obtained by evaporation at 20° C. in vacuo, and is precipitated from ethyl acetate by petroleum ether in the form of a thick oil solidifying to a vitreous mass.

Rubber ozonide is soluble in ethyl acetate, benzene and alcohol; explosive and like ozone it acts on a photographic plate.

Analysis gave the average composition C 49 per cent., H 6·9 per cent., and the molecular weight about 526, corresponding to the compound

$C_{10}H_{16}O_6$ (C 51·72 per cent., H_2 6·70 per cent., m.w. = 464).

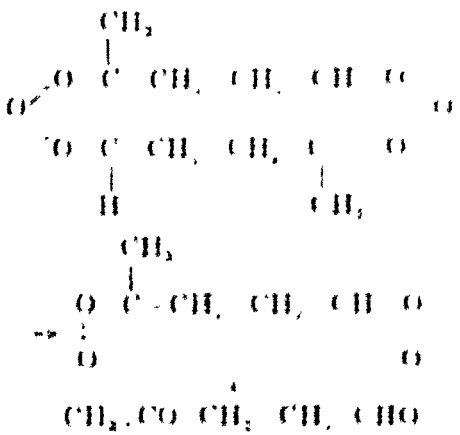
Adopting Harries' structural formula for isoprene rubber—

$$\left[\begin{matrix} CH_2C & CH_2 & CH_2 & CH \\ \| & & & \\ HC & CH_2 & CH_2 & C.CH_3 \end{matrix}\right]_x,$$

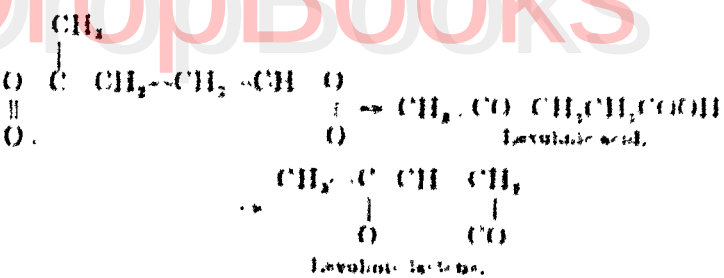
the rubber ozonide would possess the following structure:—

$$\left[\begin{matrix} & CH_2 & & H & \\ O & C & CH_2 & CH_2 & C & \\ & & & & & O \\ O & C & CH_2 & CH_2 & C & O \\ & H & & & CH_3 & \end{matrix}\right]_x.$$

Rubber ozonide suffers decomposition on boiling with water, forming levulinic aldehyde and levulinic aldehyde peroxide, as indicated by the following equation:—



On continued boiling of the aqueous solution the levulinic aldehyde peroxide undergoes autoxidation to levulinic acid, and the α and β lactones of this acid



Levulinic acid.

Levulinic lactone.

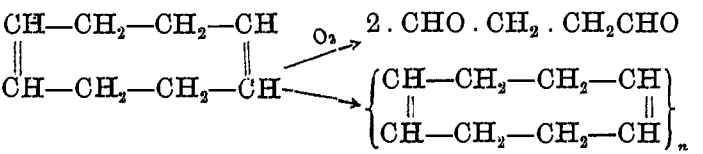
Gottlob ("Zeit. f. Anal. Chem.," **20**, 2213, 1907) investigated the action of ozone on many varieties of African rubbers, especially those from Uganda and the Upper and Lower Congo areas; he obtained the following mean values for the decomposition products:—

	Per Cent. Yield.
Levulinic acid	49·8
,, aldehyde	25·0
,, ,, peroxide	3·8
Resin	5·0

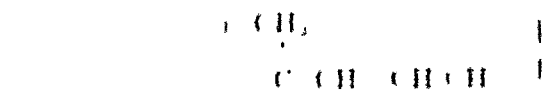
Paulsen ("Le Caoutchouc et la Guttapercha," 7, 4177, 1913) has shown that the ozonides of various resins, such as sandarac and dammar, are precipitated by carbon tetrachloride, a property which Dubosc and Luttringer ("Rubber, Its Production, Chemistry and Synthesis," Griffin, 1918) has applied to the estimation of rubber resins. Molecular weight determination has shown that the natural rubber molecule is exceedingly complex, whilst the ozonide consists of but two molecules of ozonised dimethyl cyclo octadiene. It therefore follows that ozone exerts a depolymerising action on the rubber molecule.

Attempts to prepare dimethyl octadiene itself by reduction of the ozonide have, however, proved fruitless.

Cyclo octadiene, the simplest of the cyclo octane derivations, has, however, been isolated by Willstätter, and on ozonisation and hydrolysis this yields succinic dialdehyde, whilst on polymerisation it yields a product very similar to natural rubber—



On this evidence, supported by his previous work on the nitrosites and tetrabromide of rubber, Harries adopted the somewhat unusual eight-ring structure as the unit in the polymer of natural rubber. Although Harries' views have received wide acceptation, yet this theory is contested by several workers in the field; notably by Pickles, who advances various arguments why rubber should be represented as an open-chain polymer :—



the ozonide of which would naturally possess the following structure

A few applications of the use of ozone and air have been made in preparative inorganic chemistry, the oxidation of manganates to permanganates, chlorates to perchlorates, ferrous chloride to ferric chloride are reactions which proceed smoothly and rapidly with the aid of ozone. The preparation of permanganates by means of ozone and air possesses advantages over the usual chemical method of manufacture.

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Application to Brewing and Beer Preservation.

Ozonised air has found increasing application in the brewery, not only to prevent the ingress of adventitious micro-organisms during the process of fermentation and cooling of the wort, but also the refrigerating and bottling the beer. By enclosure of the fermenting tuns and the cascade coolers in a suitable air shaft high concentrations of ozone may be used, which ensures the sterility of the air in contact with the liquid. Minor applications are found in the treatment of filtering material, the cleansing of clarifying chips and the sterilisation of bottles and casks.

According to V. Vetter (*Zeit. f. Brauerei*, Feb., 1911) all utensils, with the exception of rubber goods, which are

in the spirit, but the [illegible] part in the [illegible] of acetal produced [illegible] the presence of [illegible] the normal [illegible] spirit, as it [illegible] together with [illegible] records an [illegible] artificial [illegible] attempted on a [illegible] gators, notably [illegible] type of plant [illegible] the sterilisation of water [illegible] systems have [illegible] the ozonised air and the liquid. For the artificial [illegible] wines it is said that [illegible] utilised per hectolitre of liquid by the [illegible] cooled ozonised air for a suitable length of time. The wine so treated, it is claimed, will become fully mature in from two to three months.

For spirits some 50 litres should be utilised per hectolitre. Three days after treatment the spirit is clarified by precipitation with magnesia or filtration through suitable clarifying agents and re-ozonised, until another 50 litres of oxygen are absorbed. The process is repeated three or four times and the spirit finally stood for a few months. Villon claims that twenty year old cognac may thus be prepared in less than six months.

Although these claims are distinctly interesting, and such a method of rapidly maturing wines and spirits would possess great economic advantages, yet it must be confessed that

apart from the fact that no process of industrial ageing on these lines appears to be in actual operation, ageing is probably not entirely a process of oxidation but results from a great number of chemical reactions produced from enzyme activity taking place but slowly in the wine. Probably not the least important are the proteoclastic ferments effecting the gradual hydrolysis of the small quantities of protein substances present in the liquid.

A useful field for the application of ozonised air is to be found in the preservation of food, especially in connection with refrigeration.

For the prolonged storage of fresh meat it is necessary to maintain it at a low temperature, in order to lower the rate of hydrolysis both proteoclastic and lipoclastic produced in the meat by the naturally occurring enzyme. At normal temperatures meat can only be preserved for a few days without its quality being seriously affected by such changes occurring. During storage and transit not only are the substances subjected to internal attack by the natural enzymes but frequently external sources of contamination are to be found, especially flies and air-borne micro-organisms.

Thus maintaining perishable foodstuffs at a low temperature and in a sterile atmosphere ideal conditions for preservation obtain. Several large refrigerating warehouses and ship holds have been equipped with ozonisers on the air-circulating systems.

We have already alluded to the enhanced efficiency of ozonisers at low temperatures, hence the conjunction of an ozoniser in a refrigerating system is a particularly economical installation.

Useful applications for ozone are likewise to be found in the drying of copra, which, when subjected to the ordinary sun drying process, is liable to acquire an unpleasant empyreumatic smell. The conditioning of air in flour mills by means of ozonised air is said to be attended with a possible increase in the mill capacity of 30 per cent. and the practical elimination of the flour moth.

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CHAPTER X.

METHODS OF DETECTION AND ANALYSIS.

The presence of one part of ozone in a million of air can be detected by means of its characteristic odour, which, however, is liable to be confused with that of dilute chlorine or nitrogen peroxide.

In common with other powerful oxidising agents, it will readily liberate iodine from the usual starch iodide papers, colouring them a brilliant blue, a method employed by Schönbein, Wolffenstein and Van Bastelaer.

Houzeau indicated that by a simple modification of the test paper ozone could be distinguished from acid oxidants, such as chlorine or nitrogen peroxide. A strip of filter paper is impregnated with a solution of neutral potassium iodide and one half is then treated with starch and the other with an alkali indicator such as phenolphthalein or rosolic acid. Ozone is sharply distinguished from chlorine and nitrogen peroxide by liberating both iodine and alkali from neutral potassium iodide

$$O_3 + 2KI + H_2O = O_2 + 2KOH + I_2.$$

The paper is not entirely diagnostic for ozone, since carbon dioxide will slowly liberate iodine from neutral potassium iodide solutions and will not turn the paper distinctly acid. Hydrogen peroxide will give the same indications as ozone itself. Iodine is also set free by photolysis (Loew, "Zeit. f.

Chem. Soc. (Trans.) xciii. 1908, p. 1. The author finds that direct sunlight [illegible] ozone in presence of [illegible].

Cazeneuve has shown that [illegible] paper is [illegible] tinged from [illegible] brown coloration and the [illegible].

Arnold and Mentzel (Ber. xxxii. 1899, p. 1260) have, as a result of a series of experiments, found that [illegible] dimethyl p-phenylene diamine is better than the tetramethyl derivative (the colour [illegible] with the number of methyl groups [illegible] sensitive and at the same time [illegible] distinguishing between the different oxidizing [illegible] indicated by the following table:

Oxidant	Colour produced by Tetramethyl	Colour produced by Dimethyl
Ozone	Rose	Violet
Nitrous acid	Red	[illegible]
Halogens	Practically [illegible]	Deep blue
Hydrogen peroxide	[illegible]	[illegible]

Mention may be made of the following test papers which indicate the presence of ozone. Silver foil is coloured black by the formation of the somewhat unstable silver oxide in the presence of ozone, hydrogen sulphide will, of course, form a sulphide coloration somewhat similar to that of oxide, lead acetate paper is sufficiently diagnostic of hydrogen sulphide, whilst lead sulphide paper is bleached by ozone and hydrogen peroxide owing to conversion into lead sulphate.

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Manchot (Ber. 39, 470, 40, 289, 1907, 42, 3948, 1908) has shown that ammonia is extremely sensitive to the presence of a trace of ozone as a catalytic agent, a coloration is easily produced by 0·01 per cent ozone, and he claims this to be more sensitive than the tetramethyl base paper.

Manganese sulphate impregnated filter papers turn brown when exposed to ozone, due to the formation of Mn_2O_3. Manganese dioxide may also be formed if any alkali be present. Manganous compounds, and this in turn will undergo similar oxidation to the coloured manganese oxide, especially in the presence of light (Dunlary, "J.C.S.," 5, 1867). Thallous oxide is converted into the brown thallic oxide by the action of ozone. Nitrous acid is without effect, but acidified nitrate of thallium are not coloured. Hydrogen sulphide, however, produce a brown coloration, the former due to oxidation and the latter due to conversion into a coloured sulphide. Carbonic acid present in the gas to be detected causes a considerable decrease in sensitiveness of thallous oxide paper owing to conversion to the insoluble carbonate.

Various investigators, notably Poey and Bérigny, have used the test papers in the form of long strips in a suitable recorder mechanism for the continuous detection of ozone in gases. By means of a simple clockwork escapement a small piece of a ribbon of impregnated paper is exposed to the gas stream for a short period, and by noting the time and coloration of the paper the presence of ozone in the gas at any time during the period of operation can easily be detected.

Some attempts have been made to convert these so-called ozonoscopes into ozonometers for giving some idea as to

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Methods of Estimation

(a) Iodide Method. Ionesco's method of estimation depends on the liberation of an equivalent of iodide from a neutral solution of potassium iodide according to the equation

$$(1)\ 2KI + O_3 + H_2O = 2KOH + I_2 + O_2,$$

followed by back titration after acidification with sodium thiosulphate or sodium hydrogen sulphite, using starch as indicator, is liable to give unsatisfactory results owing to the further oxidation of the liberated iodine into chlorine iodate, and periodate (Garzarolli, "Thurnlackh Monatsh.," **22**, 455, 1901). With a large excess of potassium iodide and in a slightly acid solution, however, the possible error due to the formation of iodate and periodate is not large. According to

Ladenburg, hydrogen peroxide is formed under these conditions ("Ber.," No. 34, 1187, 1901) :—

$$2KI + 2HCl + O_3 = 2KCl + H_2O + 2O_2 + H_2O_2$$

and with which a slight loss may result, due to interaction of the ozone and the hydrogen peroxide thus formed—

$$HCl + O_3 = HCl + 2O_2$$

the results are usually somewhat higher than those determined by physical methods, which we will shortly refer to. Ladenburg ("Ber.," 36, 115, 1903) obtained excellent results by performing the estimation in the reverse manner, viz. passing ozone through standardised sodium hydrogen sulphite and back titrating with standard iodine solution.

Ingles ("J.C.S.," 98, 1010, 1903) showed that the acid iodide method invariably gave high results, neutral solutions yielding more accurate determinations. He found that neutral potassium bromide solutions gave discordant results.

Houzeau's modification of the iodine method is extremely accurate. A consideration of the equation (1) will indicate that for every equivalent of ozone two equivalents of alkali are liberated, and consequently the increase in alkalinity of the solution gives a measure of the amount of ozone. A very dilute sulphuric acid solution of potassium iodide is usually employed, followed after absorption of the ozone by back titration with standard alkali, using litmus or congo-red as an indicator. The liberated iodine can be determined in the neutral solution by means of sodium thiosulphate, thus giving a check on the former figure.

F. H. Rosenfeld and F. Bencher ("Zeit. Anorg. Chem.," 98, 167, 1916) investigated the effect of the addition of acid

to neutral potassium iodide solution for the estimation of ozone in gaseous mixtures. The reaction which gives rise to the main reaction product is represented by the equation

$$O_3 + 2KI + H_2O = O_2 + 2KOH + I_2,$$

a side reaction to a small extent being

$$O_3 + 2KI = O_2 + K_2O + I_2.$$

The side reaction would not be expected to occur to any appreciable extent in dilute solutions, but in concentrated solutions of potassium iodide, at ordinary temperatures and relatively short periods of time, as much as between 1 and 3 atoms of iodine per molecule of ozone may be obtained by titration, the exact value depending on the conditions employed. Under these conditions, however, the reaction is not readily obtainable.

They suggest that the water molecule in the KOH_2 plays a part in the reaction and that under other conditions ozone and potassium iodide may react in the following ratio as invariably obtained: KI, OH, I, for IO_2 and IO_3. The production of ozonate (O_4) in the silent electric discharge was suspected by Harries (*Ber. Deutsch. chem. Ges.* **47**, 629, 1911) as a result of analysis of the ozone obtained by the iodide method. It appears more than probable that the above side reaction fully accounts for Harries' results.

Vosmaer (*Ozone*, Constable, 1916) employs $\frac{N}{21}$ sulphuric acid, and finds that no appreciable loss of accuracy results by using acid of this strength.

(b) Arsenious Oxide Method. Thenard's method of estimating ozone, similar to that employed for evaluating bleaching powder or permanganate solutions, is based upon the oxidation of arsenious acid to arsenic acid by these oxidising agents, according to the equation :

$$4As(OH)_3 + O_2 + 3H_2O = 3As_2(OH)_8.$$

A solution of potassium arsenite is prepared by the action of arsenious oxide on sodium potassium bicarbonate, and after [illegible] titrated by $\frac{N}{1000}$ iodine solution, using starch as indicator.

The ozonised air is metered after absorption of the ozone by the potassium arsenite and arsenious acid solutions (1 wash bottle of each will suffice for flow rates up to 10 litres per hour); for higher flow rates a greater number must be employed. Hodgkinson ("Ozone and Ozonides," p. 330) states that five 1-litre wash bottles are sufficient at 600 litres per hour.

Ozone concentrations are usually expressed in grammes per cubic metre of air. It will be noted that in the case of arsenious acid absorption the equivalent volume of oxygen is not returned to the gas, as is the case in absorption by neutral potassium iodide, and consequently in this case the gas suffers a diminution in volume when passing through the absorbent; the correction, however, is but a small one. (4·8 grms. O_3 per cubic metre would give a diminution of but 0·2 per cent.)

Fischer ("Z. f. E. C.," 164, 130, 1917) suggests the use of $\frac{N}{100}$ ferrous ammonium sulphate solution, slightly acidified with sulphuric acid, as absorbent; back titration is accomplished with potassium permanganate. It is stated that the solution is unaffected by air at this concentration.

d. Physical Methods.—Otto has made use of a barograph for obtaining a continuous record of the density of a stream of ozonised air; it is claimed that the apparatus is extremely

sensitive owing to the great difference in density between ozone and oxygen. The same principle is adopted in a dilatometer for the determination of ozone based upon the increase of volume which occurs under given conditions on thermal decomposition. A 300 c.c. flask, terminating in a graduated neck, is filled at atmospheric pressure and at a given temperature with the ozonised oxygen. The flask is inverted and the graduated neck is immersed in a mercury bath, and the ozone is then decomposed by heat. Platinum foil (say 250 sq. cm.) has been found to be a suitable material for this purpose. The increase in volume after cooling to the original temperature and readjustment to the external pressure is noted and the new ozone content of the gas is calculated from the equation

$$2O_3 = 3O_2.$$

Otto further devised an optical method based on the principle of the dilatometer, more recently applied by Lovelace to similar purposes. A series of coloured cobalt-blue glasses serves as standards of comparison with a tube of definite length of ozonised air or oxygen under standard conditions of temperature and pressure.

F. Krüger and M. Moeller (*Physik. Zeit.*, 13, 771 (1912)) have suggested the measurement of ozone concentrations by the absorption of ultra-violet light. The maximum absorption of ultra-violet light by ozone is found in the region $\lambda = 200$ to 300 $\mu\mu$, especially at $\lambda = 254$ $\mu\mu$. According to Beer's law the absorption coefficient may be expressed in the form $I = I_0 e^{-kd}$ or $\log I = \log I_0 - kd$, where I_0 is the initial intensity of the ultra-violet light, I the intensity after absorption by a layer of ozonised oxygen d cms. thick containing

... and K the absorption coefficient for ... constant illumination in a tube of constant ... the ozone concentration is proportional to the ... intensity of the emergent ultra-violet light, ... by means of a potassium photo-electric cell.

... methods of physical analysis have, however, ... application, reliance having usually been ... the iodide volumetric method.

... gases containing ozone and other oxidising ... the object of investigation by Tommasi, as ... ("Chem. News," **29**, 289, 1874).

... ozone and chlorine or nitrous acid ... neutral solution of potassium ferrocyanide, ... power determined by the conversion ... ferricyanide effected. Another portion of the ... over hot platinum black, or through a hot ... manganese dioxide, when the ozone is de... The potassium ferrocyanide conversion is then determined and from the difference in the two estimates the ... of the gas can be determined.

Analysis of mixtures containing ozone and the oxides of nitrogen may also be accomplished by passing the gases into liquid air, when the oxides of nitrogen are solidified and may be separately determined.

Harries and Herfeld ("Ber.," **45**, 3575, 1912) cite an interesting method for the analysis of small quantities of methane, which, it would appear, would also be applicable to the estimation of ozone. They note that methane is quantitatively oxidised at ordinary temperatures to formaldehyde by ozone according to the equation--

$CH_4 + 2O_2 = H_2O + H_2CO_3$

It has been suggested that the method of ozone detection might be applied to the detection of electrical discharges in tunnel through which high tension electric cables are laid over the London Subway, as the amount of ozone resulting from the ionisation of the air in the tunnel would give an approximate idea of the magnitude of the electrical leak.

An instrument for the detection and measurement of small ozone in water was devised some years ago by Evans and the author ("An Electrochemical Indicator for Oxidising Agents," "The Analyst," August, 1914). The instrument consists essentially of a small cell formed by a platinum rod surrounded by a copper tube. The water containing the ozone flows through the annular space between the platinum and the copper at a good rate, and forms the electrolyte of the cell, whilst the platinum rod and the copper tube forming the electrodes of the cell are connected to a microammeter or thread recorder. In the absence of any oxidising agent in the water, the small cell rapidly becomes polarised, the current flowing through the microammeter sinks to zero, and the platinum becomes charged with hydrogen corresponding to the electrolytic solution pressure of the copper in the water. Most potable waters contain a quantity of dissolved salts to make the internal resistance of the cell sufficiently low for practical operation. On the addition of any oxidising agent to the water, the cell is partly depolarised by the removal of hydrogen from the platinum electrode, and the rate of removal of hydrogen by the ozone is measured on the microammeter.

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Since 96,540 coulombs are associated with 1 gm. equivalent or 8 gms. of ozone, assuming the electrode reaction—

$$6O \oplus O_3 = 3O'',$$

this quantity passing through the cell per second would generate a maximum current of 96,540 amperes. If the liquid flow rate were 1 c.c. per second, a fairly normal rate for the instrument, one part of ozone in 10,000,000 of water would correspond to a passage of 10^{-4} mgm. of ozone through the cell per second, equivalent to a possible current of 12×10^{-4} amperes. It is, however, evident that all the ozone cannot act as a depolariser, since half of it at least is wasted at the other electrode, and for convenience of operation the cell and flow rates are not so proportioned as to effect complete reduction of the ozone in the water flowing through the cell. In actual operation the recorded current is about 25 per cent. of the theoretical maximum. The instrument is remarkably sensitive, easily estimating or recording one part of ozone in 10,000,000 of water or ·00001 per cent.

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